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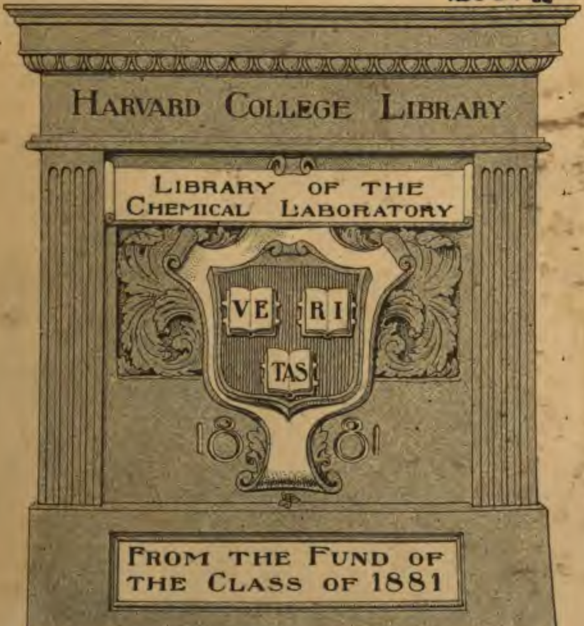

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OUTLINES

OF

QUALITATIVE CHEMICAL ANALYSIS

BY

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AND

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PREFACE.

THIS brief outline of methods in Qualitative Analysis is the outcome of many years' experience in college teaching. While it has been prepared to meet the requirements of that larger class whose concern is chiefly with the disciplinary side of the study or with general preparation for other lines of work, the needs of the specialist in exact analysis have likewise been considered. So far as possible simple methods of treatment are presented; but certainty of result under all circumstances has been made the main issue. To this end, some more elaborate processes, like the basic acetate process for the separation of aluminium, iron, and chromium from the elements of the calcium group, in presence or absence of phosphates, have been introduced in the interest of exactness as well as directness, experience having shown that the properly instructed beginner finds little difficulty and much advantage in such methods, frequently shunned in elementary work though indispensable to the practical chemist.

Among the departures from common procedure may be mentioned the use of amyl alcohol in separating strontium from calcium, of manganese chloride in strong hydrochloric acid to discover oxidizing agents, of potassium ferricyanide in distinguishing between cobalt and nickel, of iodine and bromine in testing for sulphites and thiosulphates, of a chromate with strong sulphuric acid to find a chloride in presence of a bromide, of an arsenate to indicate and separate magnesium.

Care has been taken to secure compactness in the tables of characteristic reactions, in the schemes for the systematic testing for basic ions and acidic ions, and in the statements of typical changes met with in the course of analysis. In the interest of clearness, basic and acidic ions of reaction are frequently distinguished in their symbols by the uniform use of different kinds of type; and material in the solid phase, acted upon by reagents or precipitated from solution, is similarly indicated.

To the originators of many methods taken freely from the literature and too numerous to admit of individual mention here, the authors desire to acknowledge their indebtedness.

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Page	26.			*For*	$Hg_4As_2O_6$	*read*	$Hg_3As_2O_6$
Page	29,	line	5.	“	Group I	“	Group II
“	39,	“	21.	“	$2H_2S$	“	H_2S
“	40,	“	5.	“	KCl	“	$KC_2H_3O_2$
“	“	“	10.	“	$3H_2O$	“	$6H_2O$
“	“	“	11.	“	S_2	“	S
“	“	“	21.	“	$2Sb_2S_3$	“	Sb_2S_3
“	“	“.	‘	“	S_2	“	S
“	102,	“	37.	“	C_2HO_2	“	$C_2H_3O_2$

water and alcohol; by elementary analysis, that the elements present in the mixture are carbon, hydrogen, and oxygen.

A process of analysis which rests upon the discovery of the identity of the constituents without reference to their amount is a process of *Qualitative Analysis,* while a process which has to do both with the identity and with the amounts of the constituents is a process of *Quantitative Analysis.* We find by processes of qualitative analysis that water consists of hydrogen and oxygen, and by processes of quantitative

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PART I.

INTRODUCTORY.

PRINCIPLES AND PROCEDURE.

CHEMICAL ANALYSIS is that department of chemistry which has to do with processes by which substances are identified and by which the constituents of complex substances are discovered. When the identified and recognized constituents of the substances are chemical elements, the process of determination falls under the term *elementary analysis;* when the process of determination stops with constituent compounds, it is a process of *proximate analysis.* For example, we may find by proximate analysis that a given mixture contains water and alcohol; by elementary analysis, that the elements present in the mixture are carbon, hydrogen, and oxygen.

A process of analysis which rests upon the discovery of the identity of the constituents without reference to their amount is a process of *Qualitative Analysis,* while a process which has to do both with the identity and with the amounts of the constituents is a process of *Quantitative Analysis.* We find by processes of qualitative analysis that water consists of hydrogen and oxygen, and by processes of quantitative analysis we determine the fact that water consists of 11.18 per cent of hydrogen and 88.82 per cent of oxygen by weight.

Qualitative Analysis, the special subject of our study, is more frequently proximate than elementary, since, the determination of the elementary composition of a compound once made, the recognition of a compound implies knowledge of the elementary constituents.

Any special *properties* of substances which vary with the nature of the substances are available for purposes of identification. Such are certain *properties of condition*—such as state of aggregation, color, specific gravity, refractive power for light, electrical conductivity, and other similar attributes, which, like the melting of ice or the boiling of water at definite temperature and pressure, and the color, specific gravity, and refractive power of water under defined conditions, may be observed and measured. Such also are certain *properties of reaction*, or manifestation of capacity to change chemically under changed conditions of energy, or to enter into action with other substances with the formation of new substances—like the dissociation of calcium carbonate to calcium oxide and carbon dioxide, when sufficiently heated under suitable pressure; and the action of water and iron upon one another, with formation of iron oxide and hydrogen. It is the sum total of all its properties which fixes absolutely the identity of a substance, but the determination of a small number of properties is frequently enough to make the recognition of a substance reasonably sure. The most important characteristics available for the identification and recognition of substances are found in their chemical behavior. By the judicious study of the chemical reactions into which they enter, and of the new substances thus formed, substances may be most advantageously recognized. Furthermore, since the *ions*, or parts which move from compound to compound, are the entities most in evidence in the changes which substances undergo, *qualitative analysis is chiefly concerned with the recognition of the ions of reaction.*

Common phenomena for which we look in reactions as evidence of the formation of new substances are the production of a new state of aggregation and new properties, or the development of new physical properties pertaining to the substance apparently unchanged in state. So we look for a change of solids to the liquid or gaseous condition, for a change of liquids to the solid or gaseous condition, for a change of gases to the solid or liquid condition. We look also for the development of new properties such as a change of the amorphous condition or of the crystalline condition of solids, a change of the viscosity or fluidity of liquids, or a change of the density of gases. Changes of color in solids, liquids, and gases are likewise often marked and distinctive characteristics; but it must not be forgotten that the color of an individual substance may vary greatly with its fineness of subdivision or mode of production. Polished copper, for example, is very different in color and general appearance from copper deposited from solution by the action of a more electropositive metal, and the color of electrolytically deposited copper varies with the strength of current and other conditions of the deposition.

Chemical reactions may be brought about in individual substances by changes in conditions of energy, as in the case just cited, in which calcium carbonate breaks up into calcium oxide and carbon dioxide under the influence of heat. Chemical reactions between two or more substances take place only when the substances are in close contact, though such reactions may either be spontaneous, as soon as contact is effected, or they may be established only by certain changes of energy, as by accession of heat or application of an electric current. Given suitable conditions of energy for spontaneous reaction, facility of contact favors chemical activity.

Between gases and between miscible liquids chemical reaction takes place easily and thoroughly; between solids chemical reaction is limited and difficult. When, therefore, we wish to bring about reactions between solid substances, we usually gasify them by adjusting the conditions of temperature and pressure, or we liquefy them by fusion or by dissolving them in a suitable solvent. Sometimes it is sufficient to gasify or liquefy one of the reacting substances, providing the products of reaction are gaseous or soluble, and so continuously removed from the contact surface of the solid substance. Some chemical reactions, like the reduction of copper oxide by hydrogen at moderately high temperatures, are *complete reactions*—that is, they proceed under defined conditions of energy until one or more of the reacting substances is used up. But many chemical reactions, taking place under defined conditions of energy, are, like the reduction of iron oxide by hydrogen in a closed space, *incomplete reactions*—that is, they proceed to a condition of equilibrium between active substances. By removing from the system an active product as it is formed, an incomplete reaction may be made complete; or, by properly concentrating a certain factor of the reaction (taking advantage of the principle of mass-action), an incomplete reaction may frequently be pushed onward toward completion. Thus in reducing ferric oxide by hydrogen taken in equivalent proportions in a closed vessel the reaction comes to an equilibrium:

$$Fe_2O_3 + 3H_2 \rightleftarrows 2Fe + 3H_2O.$$

If the iron oxide is heated in a tube through which hydrogen is passed, the water formed is swept away in the current of hydrogen, and the reduction is made complete; or, even when all the water is retained in the system, an increase in the proportion of the hydrogen originally present will push the reduction of the iron oxide farther.

It is generally advantageous in analytical operations to make reactions as complete as possible, that tests may be delicate and separations as nearly perfect as may be.

Reactions which take place in solution in water are of the greatest importance in analytical operations. Of such reactions, some result in the formation of a very insoluble and inactive product, and are practically complete. Others are incomplete, but may be made complete by taking steps to make a somewhat soluble and active product more insoluble and inactive. For example, if exactly the equivalent amount of sulphuric acid is added to barium chloride in solution in water, barium sulphate is precipitated, and the reaction is practically complete; for one part by weight of barium sulphate requires more than 400,000 parts of water to dissolve it. The reaction by which barium sulphate is precipitated is, nevertheless, a reversible reaction:

$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2HCl.$$

If hydrochloric acid, a product of the reaction, be added to the mixture until it amounts to three per cent of the whole solution, the reverse action sets in and continues until barium salt remains in solution to an amount twenty-two times that which dissolves in pure water, or to one part in seventeen thousand of the solution. The precipitation of barium chloride by an equivalent amount of sulphuric acid is, therefore, incomplete in presence of much hydrochloric acid; but the precipitation may be made complete in several ways.

If the solution is evaporated to dryness until the hydrochloric acid is volatilized, the residue will consist of barium sulphate practically insoluble in water. If, taking advantage of the principle of mass-action, the proportion of sulphuric acid, the precipitant and active agent by which barium chloride is converted to barium sulphate, is increased, the direct action is advanced, and is practically complete when the sulphuric acid amounts to two and a half per cent, even when the excess of hydrochloric acid makes up twenty per cent of the solution. When to the mixture of barium chloride, sulphuric acid, and the excess of hydrochloric acid, sodium hydroxide is added to neutralization, the precipitation of barium sulphate is practically complete; and sodium acetate in considerable amount accomplishes the same effect, since the acetic acid liberated in the metathesis between this salt and the free acid is inert toward barium sulphate. Another mode of completing an incomplete reaction is illustrated in the action which takes place between sulphuric acid and calcium chloride. The precipitation of calcium sulphate is far from complete in water, one part of calcium sulphate being soluble at the ordinary atmospheric temperature in four hundred parts of water; but if alcohol, to twice the volume of the mixture, is added, precipitation is almost complete:

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl.$$

These examples are typical of methods important in analytical chemistry, by which incomplete reactions in solution may be pressed onward toward completion.

Incomplete precipitations may frequently be made practically complete by the removal of an active product by volatilization, by an increase in concentration of a precipitant, by the conversion of an active product to an inert product, or by a change in the nature of the solvent.

In the specific reaction involving the mutual neutralization of an acid and a base in solution in water, the reaction may be complete or incomplete according to the nature of factors and products of the reaction. When the water formed in the reaction and the salt produced in the neutralization are mutually inactive, the reaction is complete, as when potassium hydroxide and sulphuric acid neutralize one another:

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

When the water and the salt formed are mutually active, the reaction is incomplete, as when arsenious oxide and hydriodic acid are brought together in concentrated solution in water:

$$As_2O_3 + 6HI \rightleftarrows AsI_3 + 3H_2O.$$

But such *a reaction of neutralization, incomplete because of the hydrolytic action of the product water upon another product of the reaction, may sometimes be made complete by adding some otherwise inert substance to combine with water.* The addition of sulphuric acid, otherwise inert, in ordinary amount, is capable of reversing the hydrolytic action of water in the reaction given and establishing the precipitation of arsenious iodide.

When substances occur in mixture, it is usually necessary to effect their separation in order that methods may be applied for the identification of the individual constituents of the mixture.

Gases may be separated from one another, more or less completely, by diffusion, or by the specific action of other suitable substances. Thus, hydrogen and oxygen may be partially separated by the more rapid diffusion of the former through the porous walls of the container; while carbon dioxide and air may be separated by the specific effect of potassium hydroxide upon carbon dioxide, potassium carbonate being formed. *Gases and liquids, or gases and solids, may be separated by applying heat and relieving pressure, or by the specific action of certain suitable substances.* Thus hydrogen and water dissolving it, or hydrogen and palladium in solid solution, may be parted by heating, and more easily under diminished pressure; while carbon dioxide and the water dissolving it may be parted by the action of calcium hydroxide, with formation of calcium carbonate, and the same gas absorbed in porous clay may be dissolved out of it by water.

Liquids, if non-miscible, may be separated from one anothe by decantation (pouring off, siphoning, or parting by means of a separating funnel); if miscible, by fractional distillation; or, whether miscible or non-miscible, by reaction with suitable substances. For example, water and chloroform may be fairly well parted in the separating funnel, while alcohol and water may be fairly well separated by fractional distillation. Alcohol and water are, however, more completely parted by the action of calcium oxide, with formation of calcium hydroxide; and the last traces of water may be taken out of alcohol by the regulated action of sodium, which decomposes the water with formation of sodium hydroxide and hydrogen.

Solids and liquids may be separated by distillation of the latter; or, partially, if the solids are insoluble, by decantation or filtration; or, partially, if the solids are soluble, by converting dissolved substances into insoluble substances and then decanting or filtering. So, muddy water is purified by distilling it, leaving behind both the suspended and the dissolved solids; water and suspended dust may be separated by filtration; and water and the dissolved matter which makes it "temporarily hard" may be separated by adding to the solution just enough calcium hydroxide to react with the dissolved calcium hydrogen carbonate to form calcium carbonate, from which the water may be decanted or filtered. *When solids and liquids are partially separated by decantation or filtration, the separation may be completed by evaporating the last portions of the liquids, or by washing the solids with some other liquid which may remove the last portions of the first liquid and then be itself evaporated.* For example, solid chromium trioxide and the liquid sulphuric acid which throws it down from a solution of chromic acid may be separated partially by filtration on asbestos; the last portions of sulphuric acid may be removed by washing the solid chromic trioxide upon the asbestos with strong nitric acid; and the nitric acid which adheres to the chromium trioxide may be removed by evaporation at a low temperature, best under diminished pressure, leaving the completely separated chromium trioxide.

Solids in mixture may sometimes be separated from one another by suspension, flotation, or fanning; sometimes by suitable solvents; and sometimes by the action of suitable chemical reagents. Minerals are sometimes separated and prepared for analysis by the suspension of the lighter constituents in liquids of suitable density, which permit the heavier substances to sink. Gold, in the gold-washings, is separated from sand by the flotation of the lighter particles in running water. Grain is winnowed from the chaff by fanning with air. Sand and sugar may be separated by the solvent action of water upon the sugar. Silver and gold in alloy may be parted by nitric acid, which acts upon the silver and leaves the gold.

It is to be noted that processes of washing, whether by decantation or by filtration, are the more effective for a given amount of washing liquid when this is applied in successive portions large relatively to the residue to which each portion is applied. For example, given a mass of sand covered by 200 $cm.^3$ of solution, we may get an idea of the relative effectiveness of different methods of applying a given amount of wash-water. If, first, 100 $cm.^3$ of the solution is decanted, one-half of the soluble matter will be removed. Successive washings by filling to 200 cm.^{3}, mixing, settling, and pouring off 100 cm.^{3} will remove each time one-half of the soluble matter at that time in the solution. The application in this manner of 900 cm.^{3} of water in portions of 100 cm.^{3} will result in leaving $\frac{1}{2^{10}}=\frac{1}{1024}$ of the soluble matter of the solution, provided the soluble matter is uniformly distributed through the liquid every time a new portion of wash-water is applied.

If, on the other hand, nine-tenths of the liquid is poured off in the first decantation, leaving $\frac{1}{10}$ of the soluble matter originally present; the remaining 20 cm.^{3} diluted to 200 cm.^{3}; the solution mixed, settled, and poured off until only 20 cm.^{3} remain; then $\frac{1}{10}$ of $\frac{1}{10}$ of the original soluble material will be left. After washing in this manner by 900 cm.^{3} of water applied in five portions, the amount of solid matter in solution will be $\frac{1}{10^6}=\frac{1}{1,000,000}$ of that originally present in solution. The second method of applying the given volume of water is obviously nearly a thousand times as effective as the first method.

As a matter of fact, the washing of insoluble material is never so complete as would be indicated by our theory, for the reason that the distribution of soluble material in a mixture of solid and solution is never uniform throughout the given volume, portions of the solution being concentrated within the pores of the solid, or upon its surface by what is known as adsorption. To remove sulphuric acid from spongy silver, for example, in a well-known analytical process, requires not merely superficial washing of the silver, but intervals of soaking, in order that the included acid may diffuse from the silver into the wash-water. The ease with which a solid may be washed depends largely upon its condition. Granular material is more easily washed than colloidal material, and the more easily as the grains are larger.

In analytical processes the substances to be washed are generally precipitates, and upon their character depends the ease of the operation. Crystalline precipitates may generally be washed easily, but some crystalline precipitates are so finely divided that they make difficulty by their tendency to clog the filter and even to pass through the pores of the filter. Such precipitates, of which calcium oxalate is an example, may be handled better if allowed to digest for some time in contact with the liquid from which they have been formed; for all are more or less soluble, and in the continual reaction between solvent and solute the larger grains tend to grow larger and the smaller particles to disappear, and warmth is usually favorable to such action.

Colloidal precipitates not only tend to clog the filter, but, as the material in solution diminishes in the process of washing, to disintegrate. Precipitates of this sort are best washed toward the end of the operation with a solution of some salt as little disadvantageous as may be in subsequent operations. Stannic sulphide, such a precipitate, is often washed with a solution of ammonium nitrate, a substance easily volatilized afterward, if need be.

Filters of paper are most frequently employed in analytical operations, but asbestos is often serviceable, especially in filtering strong acids or solutions of alkali hydroxides. Suction is sometimes used to make filtration more rapid, but the filter-paper must then be protected and supported in the funnel by little perforated cones of platinum or of parchment.

CLASSIFICATION OF THE IONS OF REACTION.

Ions are classified as positive or basic, and negative or acidic.

A. Grouping of Positive or Basic Ions.

Basic ions are classified in groups, as follows:

Group I. Basic ions whose soluble compounds form with hydrochloric acid *insoluble chlorides:*

Ag, Hg_2, *Pb.

Group II. Basic ions which do not yield insoluble chlorides, but whose soluble compounds form with hydrogen sulphide in the presence of dilute hydrochloric acid *insoluble sulphides:*

Pb, Hg, Bi, Cu, Cd, As, Sb, Sn.

Division A. Ions forming sulphides insoluble in ammonium polysulphide:

Pb, Hg, Bi, Cu, Cd.

Division B. Ions forming sulphides soluble in ammonium polysulphide:

As, Sb, Sn.

Group III. Basic ions which do not yield insoluble chlorides nor insoluble sulphides in the presence of free dilute hydrochloric acid, whose compounds form with ammonium hydroxide *hydroxides* insoluble in faint excess of the precipitant and in ammonium salts, and whose acetates are hydrolyzed when heated, with formation of *insoluble basic acetates:*

---

* Lead chloride is partially soluble even in cold water and not completely separated.

Al, Fe^{III}, Cr^{III}.

Group IV. Basic ions which do not yield insoluble chlorides, sulphides in the presence of dilute hydrochloric acid, hydroxides in the presence of ammonium salts, or basic acetates, but whose soluble compounds form with ammonium sulphide *insoluble sulphides:*

Ni, Co, Fe^{II}, Mn, Zn.

Group V. Basic ions which do not yield insoluble chlorides, sulphides, or hydroxides in the presence of ammonium salts, but whose compounds form with ammonium carbonate in the presence of moderate amounts of ammonium salt *insoluble carbonates:*

Ba, Sr, Ca.

Group VI. Basic ions which do not yield insoluble chlorides, sulphides, hydroxides, or carbonates in the presence of ammonium salts:

Mg, NH_4, Na, K, Li.

B. Grouping of Negative or Acidic Ions.

The acidic ions naturally divide into three groups:

Group I. Acidic ions whose soluble compounds form precipitates with barium chloride or barium nitrate in neutral solutions not containing salts of ammonium *:

---

* The silver compounds of some of these ions are precipitated from neutral solutions by silver nitrate, but the salts thus thrown down are soluble in nitric acid.

SO_4 SiF_6	Yielding barium salts insoluble in dilute hydrochloric acid or nitric acid.
PO_4 AsO_4 BO_3 AsO_3 C_2O_4 $C_4O_6H_4$ F	Yielding barium salts soluble in dilute hydrochloric acid or nitric acid without any apparent decomposition.
CO_3 SO_3 S_2O_3 CrO_4 SiO_4	Yielding barium salts soluble in dilute hydrochloric acid or nitric acid with evident decomposition.

Group II. Acidic ions whose soluble compounds form precipitates with silver nitrate in solutions acidified with nitric acid *:

Cl
Br
I
CN
$Fe^{\text{II}}C_6N_6$
$Fe^{\text{III}}C_6N_6$
SCN
S
(NO_2)

Group III. Acidic ions whose barium compounds and silver compounds are soluble even in water:

ClO_3
ClO
NO_3
NO_2
C_2H_3O

---

* The barium salts containing these ions are soluble either in neutral or in acid solution.

PART II.

THE BASIC ANALYSIS.

REACTIONS AND METHODS.

THE Basic Analysis is that part of Qualitative Analysis which treats of the identification of the Positive or Basic Ions.

CHARACTERISTIC REACTIONS OF BASIC IONS.

GROUP I.

TYPICAL COMPOUND. REAGENT.	$AgNO_3$	$Hg_2(NO_3)_2$	$Pb(NO_3)_2$
HCl	P. white, curdy $\mathbf{AgCl}$. Insol. in acids. Sol. in NH_4OH. " KCN. " $Na_2S_2O_3$. Darkens in the light.	P. white, granular $\mathbf{Hg_2Cl_2}$. Insol. in cold HCl. Sol. in HNO_3. " aqua regia. Converted by ammonia into $\mathbf{NHg_2Cl.NH_4Cl + 2Hg}$ with blackening.	P. white, Xn. $\mathbf{PbCl_2}$. Slightly sol. in *cold* water, *freely* in *hot* water. With NH_4OH gives an insoluble basic salt.
H_2S	P. black $\mathbf{Ag_2S}$. Insol. in $(NH_4)_2S$. Sol. in hot HNO_3.	P. black $\mathbf{HgS + Hg}$. Partly sol. in HNO_3. Sol. in aqua regia.	P. black $\mathbf{PbS}$. In presence of much HCl red lead chlorosulphide $\left(\begin{matrix} x\ \mathbf{PbCl_2} \\ y\ \mathbf{PbS} \end{matrix}\right)$ may fall first, which by excess of H_2S is converted into *black* $\mathbf{PbS}$. Insol. in $(NH_4)_2S$. Sol. in HNO_3.
H_2SO_4	P. white $\mathbf{Ag_2SO_4}$, only in concentrated solutions.	P. white $\mathbf{Hg_2SO_4}$. Slightly sol. in water.	P. white $\mathbf{PbSO_4}$. Insol. in dilute H_2SO_4. Somewhat sol. in HNO_3. Sol. in $NH_4C_2H_3O_2$ and in $NaOH$.
$NaOH$	P. brown $\mathbf{Ag_2O}$. Sol. in HNO_3. " NH_4OH.	P. black $\mathbf{Hg_2O}$. Sol. in HNO_3. Insol. in NH_4OH.	P. white $\mathbf{PbO_2H_2}$. Sol. in excess of $NaOH$. Sol. in HNO_3. Insol. in NH_4OH.

CHARACTERISTIC REACTIONS OF BASIC IONS.

GROUP I.

TYPICAL COMPOUND. REAGENT.	$AgNO_3$	$Hg_2(NO_3)_2$	$Pb(NO_3)_2$
NH_4OH	P. brown Ag_2O. Sol. in excess of NH_4OH.	P. black amine, *e.g.* NHg_2NO_3+2Hg. Nearly insol. in excess of NH_4OH.	P. white basic salt. Insol. in excess of NH_4OH.
Na_2CO_3	P. white Ag_2CO_3. Sol. in NH_4OH.	P. yellow basic carbonate going into Hg_2O and blackening.	P. white basic carbonate, *e.g.* $2PbCO_3+PbO_2H_2$, "white lead."
K_2CrO_4	P. dark red Ag_2CrO_4. Sol. in HNO_3, in NH_4OH.	P. dark red basic salt. Slightly sol. in HNO_3.	P. yellow $PbCrO_4$. Somewhat sol. in HNO_3.
$K_4FeC_6N_6$	P. white $Ag_4FeC_6N_6$. Insol. in NH_4OH.	P. white $(Hg_2)_2FeC_6N_6$.	P. white $Pb_2FeC_6N_6$.
$SnCl_2$	P. white AgCl.	P. dark gray Hg.	P. white $PbCl_2$.

SEPARATION AND IDENTIFICATION

To the solution containing silver, mercurous, and lead salts add hydrochl

Precipitate (1)

AgCl, Hg_2Cl_2, $PbCl_2$.

Treat on the filter with a small amount of boiling

Residue (2)

AgCl, Hg_2Cl_2.

Wash thoroughly with hot water, until the washings give no test for *Pb.* Moisten thoroughly but not too copiously with NH_4OH, and wash with a little water.

Residue (3)

$NHg_2Cl.NH_4Cl+2Hg$.

Black coloration indicates the formation of **$NHg_2Cl.NH_4Cl+2Hg$.** Perforate the filter, wash into a test-tube, dissolve in a very little aqua regia, dilute, filter (to remove any AgCl still remaining), and add $SnCl_2$.

P. white, **Hg_2Cl_2**, or gray or dark **Hg_2Cl_2+Hg**, indicates [*Hg_2*].

TABULAR VIEW OF GROUP I.

Typical Compound.	Treatment with HCl.	Treatment of P (1) with Hot Water.		Treatment of R (2) with NH_4OH.	
	P (1)	R (2)	F (2)	R (3)	F (3)
$AgNO_3$	AgCl	AgCl			xAgCl.$y$$NH_3$
$Hg_2(NO_3)_2$	Hg_2Cl_2	Hg_2Cl_2		$NHg_2Cl.NH_4Cl+2Hg$	
$Pb(NO_3)_2$	$PbCl_2$		$PbCl_2$	....	

OF BASIC IONS OF GROUP I.

oric acid in excess, but not in great excess, filter, and wash with cold water.

Filtrate (1)

Reject.

water.

Filtrate (2)

$PbCl_2$.

Divide in three portions:
(1) Add K_2CrO_4. P. yellow **$PbCrO_4$** indicates *Pb*.
(2) Add KI. P. yellow **PbI_2** soluble in hot water, indicates *Pb*.
(3) Add H_2S. P. black **PbS** indicates *Pb*.

Filtrate (3)

$x\ AgCl.y\ NH_3$.

Add dilute HNO_3 to faint acidity.

P. white, curdy on shaking, **AgCl**, indicates *Ag*.

If the extraction by hot water was imperfect, lead may remain to dissolve in the excess of ammonia and appear on adding HNO_3. It will, however, dissolve in a slight excess of HNO_3, leaving the AgCl.

COMMENTARY UPON GROUP I.

Group I is distinguished by the insolubility of its chlorides in water, though lead chloride is slightly soluble in cold water and freely soluble in hot water, and so is not completely separated.

A reasonable excess of hydrochloric acid should be used in precipitating the chlorides in order to insure the complete precipitation of the silver chloride and mercurous chloride. A large excess of the acid is to be avoided on account of its solvent action, especially upon the silver chloride.

The washing of the precipitated chlorides with water is to remove soluble compounds, and cold water is used in order to avoid the increased solvent action which warm water has upon lead chloride.

In separating lead chloride from the other chlorides of this group, use is made of the solvent action of hot water. It is used in small amount first, to insure a fairly concentrated solution of lead chloride for the lead tests. The complete removal of lead chloride from the other chlorides is readily accomplished by continued treatment with hot water without any appreciable effect upon the other salts.

The residual chlorides, when acted upon by ammonium hydroxide, give a black insoluble mixture of the dimercurammonium double salt and mercury, and a soluble silver compound. The ammoniacal silver solution is readily decomposed by nitric acid with the reprecipitation of silver chloride. A large excess of ammonium hydroxide in effecting this separation tends to produce some solvent action upon the mercury compound and so should be avoided.

If the amount of silver chloride present is small relatively to the amount of mercurous chloride, it may be reduced to metallic silver by the metallic mercury in the black residue. If no silver has been found when the formation of the black residue is large, this residue may, if desired, be further examined for traces of silver by volatilizing the mercury (under a hood), dissolving the residue in nitric acid, and precipitating by hydrochloric acid.

Important Reactions.

$Pb(NO_3)_2 + 2HCl = \mathbf{PbCl_2} + 2HNO_3.$
$PbCl_2 + K_2CrO_4 = \mathbf{PbCrO_4} + 2KCl.$
$PbCl_2 + H_2S = \mathbf{PbS} + 2HCl.$
$PbCl_2 + H_2SO_4 = \mathbf{PbSO_4} + 2HCl.$
$PbCl_2 + 2KI = \mathbf{PbI_2} + 2KCl.$

$AgNO_3 + HCl = \mathbf{AgCl} + HNO_3.$
$x\,\mathbf{AgCl} + y\,NH_4OH = x\,AgCl.y\,NH_3 + y\,H_2O.$
$x\,AgCl.y\,NH_3 + y\,HNO_3 = x\,\mathbf{AgCl} + y\,NH_4NO_3.$

$Hg_2(NO_3)_2 + 2HCl = \mathbf{Hg_2Cl_2} + 2HNO_3.$
$\mathbf{2Hg_2Cl_2} + 4NH_4OH = \mathbf{NHg_2Cl.NH_4Cl} + \mathbf{2Hg} + 2NH_4Cl + 4H_2O.$
$\mathbf{2Hg} + \mathbf{NHg_2Cl} + 4HCl + 2Cl_2 = 4HgCl_2 + NH_4Cl.$
$3HgCl_2 + 2SnCl_2 = 2SnCl_4 + \mathbf{Hg_2Cl_2} + \mathbf{Hg}.$

CHARACTERISTIC REACTIONS OF BASIC IONS.

Group II. Division A.

Typical Compound. Reagent.	*Hg*Cl_2	*Cu*Cl_2	*Bi*Cl_3	*Cd*Cl_2
*H*Cl	....	....	....	....
H_2S	P. black **HgS**. At first a white chlorosulphide $\left(\begin{matrix} x\ \mathbf{HgCl_2} \\ y\ \mathbf{HgS} \end{matrix}\right)$ may form, which shows gradations of color as action of H_2S continues, and becomes black **HgS**. Insol. in $(NH_4)_2S$. Insol. in HNO_3, sometimes turning white. Sol. in aqua regia.	P. black **CuS**. Sol. in HNO_3, very slightly in $(NH_4)_2S$. Insol. in hot dilute H_2SO_4, 1:6.	P. black or dark brown $\mathbf{Bi_2S_3}$. Insol. in $(NH_4)_2S$. Sol. in HNO_3.	P. yellow **CdS**. Insol. in $(NH_4)_2S$. Sol. in HNO_3. Sol. in hot dilute H_2SO_4, 1:6.
H_2SO_4	....	....	P. white, sometimes deposited on long standing.	....
*Na*OH	P. yellow **HgO**. Sol. in HNO_3. In presence of NH_4Cl the white compound $\mathbf{NHg_2Cl.NH_4Cl}$ is formed.	P. bluish $\mathbf{CuO_2H_2}$. Goes upon boiling into black **CuO**. Sol. in HNO_3. " NH_4OH.	P. white **BiO(OH)**. Sol. in HNO_3. Insol. in NH_4OH.	P. white $\mathbf{CdO_2H_2}$. Sol. in HNO_3. " NH_4OH.

CHARACTERISTIC REACTIONS OF BASIC IONS.

Group II. Division A (*Concluded*).

Typical Compound. Reagent.	*Hg*Cl_2	*Cu*Cl_2	*Bi*Cl_3	*Cd*Cl_2
NH$_4$OH	P. white **$NHg_2Cl.NH_4Cl$**. Sol. in HCl. [Not precipitated if much free acid is present originally.]	P. greenish blue basic salt. Sol. in excess of NH_4OH to a blue solution.	P. white **BiO(OH)**. Insol. in excess of NH_4OH.	P. white **CdO_2H_2**. Sol. in excess of NH_4OH.
Na$_2CO_3$	P. reddish brown oxychloride, **$nHgCl_2.HgO$**. On boiling goes into **HgO**.	P. bluish basic carbonate **$mCuCO_3.nCuO_2H_2$**. Goes into black **CuO** on boiling.	P. white basic carbonate **$Bi_4(OH)_2O_3(CO_3)_2$**.	P. white **$CdCO_3$**.
K$_2CrO_4$	P. reddish yellow **$HgCrO_4$**. Sol. in HNO_3.	P. reddish brown **$CuCrO_4$** in neutral solutions. Sol. in NH_4OH to a green solution.	P. yellow **$Bi_2O(CrO_4)_2$**. Sol. in HNO_3.	P. yellow, slightly sol. in water, sol. in acids.
K$_4FeC_6N_6$	P. white, becoming bluish on long standing.	P. mahogany-brown **$Cu_2FeC_6N_6$**. Insol. in acid. Slightly sol. in NH_4OH.	P. pale yellow. Sol. in HCl.	P. nearly white **$Cd_2FeC_6N_6$**. Sol. in HCl.
SnCl_2	P. white **Hg_2Cl_2** or gray **Hg_2Cl_2+Hg**.	P. only in concentrated solution, white **Cu_2Cl_2**.	No action on acid solution, but when NaOH is added black **Bi** is formed.	....
H_2O	....	....	P. white **BiOCl**.	

CHARACTERISTIC REACTIONS

GROUP II.

TYPICAL COMPOUND. REAGENT.	H_3AsO_3	H_3AsO_4	$SnCl_2$
H_2S	P. yellow **As_2S_3**. Insol. in concentrated HCl. Sol. in alkali hydroxides and sulphides.	P. yellow **As_2S_5** or $As_2S_3 + S_2$. Forms slowly on warming. Insol. in HCl. Sol. in alkali hydroxides and sulphides.	P. dark brown **SnS**. Sol. in concentrated HCl. Sol. in alkali sulphides containing free sulphur. Sol. with difficulty in alkali hydroxides. Difficultly sol. in alkali sulphides with *no* free S.
$(NH_4)_2S+S$	P. yellow **As_2S_3**. Sol. in excess, forming $(NH_4)_3AsS_4$.	P. yellow **As_2S_5**. Sol. in excess, forming $(NH_4)_3AsS_4$.	P. dark brown **SnS**. Sol. with difficulty in excess. Sol. on addition of S, forming $(NH_4)_2SnS_3$.
NaOH	....	....	P. white **SnO_2H_2**. Sol. in excess.
NH_4OH	....	....	P. white **SnO_2H_2**. Darkens in excess on boiling.

OF BASIC IONS.

DIVISION B.

$SnCl_4$	$SbCl_3$	$SbCl_5$	TYPICAL COMPOUND.
			REAGENT.
P. yellow SnS_2. Sol. in concentrated HCl. Sol. in alkali hydroxides and sulphides.	P. orange Sb_2S_3. Sol. in concentrated HCl. Sol. in alkali hydroxides and sulphides.	P. light orange Sb_2S_5 or $Sb_2S_3 + S_2$. Sol. in concentrated HCl. Sol. in alkali hydroxides and sulphides.	H_2S
P. yellow SnS_2. Sol. in excess, forming $(NH_4)_2SnS_3$.	P. orange Sb_2S_3. Sol. in excess, forming $(NH_4)_3SbS_4$.	P. light orange Sb_2S_5. Sol. in excess, forming $(NH_4)_3SbS_4$.	$(NH_4)_2S+S$
P. white SnO_4H_4. Nearly completely sol. in *slight* excess.	P. white SbO_3H_3. Sol. in excess.	P. white $NaSbO_3$. Sol. in excess, especially on heating. [$KOSbO_2$ is more sol.]	$NaOH$
P. white SnO_4H_4. Slightly sol. in excess.	P. white SbO_3H_3. Insol. in excess.	P. white NH_4SbO_3. Nearly insol. in excess.	NH_4OH

CHARACTERISTIC REACTIONS

GROUP II.

<table>
<tr><th>TYPICAL COMPOUND.</th><th>H_3AsO_3</th><th>H_3AsO_4</th><th>$SnCl_2$</th></tr>
<tr><td>REAGENT.
Na_2CO_3</td><td>........</td><td>........</td><td>P. white SnO_2H_2. Insol. in excess.</td></tr>
<tr><td>$AgNO_3$</td><td>P. yellow Ag_3AsO_3. Sol. in HNO_3 and in NH_4OH.</td><td>P. brick-red Ag_3AsO_4. Sol. in HNO_3, in NH_4OH.</td><td>P. white AgCl, or dirty white AgCl+Ag.</td></tr>
<tr><td>$HgCl_2$</td><td>P. white $Hg_4As_2O_6$. Sol. in acids.</td><td>........</td><td>P. white Hg_2Cl_2 or gray Hg_2Cl_2+Hg.</td></tr>
<tr><td>Mg mixture
$MgCl_2$
NH_4Cl
NH_4OH</td><td>........</td><td>P. white NH_4MgAsO_4. Sol. in acids, even in $HC_2H_3O_2$.</td><td>P. white SnO_2H_2. Insol. in excess—as with NH_4OH.</td></tr>
<tr><td>Nascent H in acid sol. (Zn+HCl)</td><td colspan="2">Gaseous AsH_3.
Yields deposit of As in hot tube or on porcelain sol. in NaOCl, also in $(NH_4)_2S$+S and the sol. in the latter gives with HCl, P. yellow As_2S_5.</td><td>P. gray. Metallic Sn.</td></tr>
<tr><td>H_2O</td><td>........</td><td>........</td><td>........</td></tr>
</table>

OF BASIC IONS.

DIVISION B (*Concluded*).

$SnCl_4$	$SbCl_3$	$SbCl_5$	TYPICAL COMPOUND.
P. white SnO_4H_4. Insol. in excess.	P. white SbO_3H_3. Somewhat sol. in excess. On boiling tends to throw down Sb_2O_3.	P. white $NaSbO_3$. Sol. in excess, especially on boiling.	**REAGENT.** Na_2CO_3
P. white AgCl.	P. white AgCl. Sol. in NH_4OH. Sb_2O_3, insol. in NH_4OH.	P. white AgCl, and on neutralizing the solution, white Ag_3SbO_4. Sol. in NH_4OH.	$AgNO_3$
....	....	....	$HgCl_2$
P. white SnO_4H_4. Slightly sol. in excess—as with NH_4OH.	P. white SbO_3H_3. Insol. in excess—as with NH_4OH.	P. white NH_4SbO_3. Nearly insol. in excess—as with NH_4OH.	Mg mixture $MgCl_2$ NH_4Cl NH_4OH
P. gray. Sn, and, from sol. exhausted of acid, SnO_3H_2	Black stain or deposit and gaseous SbH_3. Deposit of Sb in hot tubes or on porcelain insol. in dilute NaOCl; sol. in $(NH_4)_2S+S$, and this solution gives Sb_2S_5 with HCl.		Nascent H in acid sol. (Zn + HCl)
....	P. white SbOCl.	P. white ($SbOCl_3$, etc.) H_3SbO_4.	H_2O

SEPARATION AND IDENTIFICATION OF

Acidify the solution containing members of this group with HCl, warm, four times and pass H_2S. Should further precipitation take place in this dilution and treatment with H_2S no effect is produced. Wash the precipitate

Precipitate (1), DIVISIONS A and B.—HgS, PbS, Bi_2S_3, CuS, CdS, SnS, SnS_2, Sb_2S_3, Sb_2S_5, As_2S_3, As_2S_5. Transfer to a test-tube or small beaker, add 5 to 10 cm.^{3} of ammonium polysulphide $(NH_4)_2S+S$, warm gently, dilute, settle, and filter.

DIVISION A. *Residue* (2).—HgS, PbS, Bi_2S_3, CuS, CdS. Wash thoroughly, perforate the filter, transfer to a test-tube with dilute HNO_3 (usually about 5 cm.^{3}), and boil as long as anything appears to dissolve. Dilute and filter.

Residue (3).—Black HgS, or white $HgS.Hg(NO_3)_2$, or, possibly $PbSO_4$. Dissolve in a little aqua regia, dilute, filter, and add $SnCl_2$. P. white Hg_2Cl_2, or gray or dark Hg_2Cl_2+Hg, indicates *Hg*.

Precipitate (4).—White $PbSO_4$. Confirm by dissolving in NaOH, adding K_2CrO_4, and acidifying with $HC_2H_3O_2$. P. yellow $PbCrO_4$ indicates *Pb*.

Precipitate (5).—White $BiO(OH)$. Dissolve in two or three drops of dilute HCl and let the solution drop into 10 or 20 cm.^{3} of water. P. white $BiOCl$ indicates *Bi*.

BASIC IONS OF GROUP II. DIVISION A.

pass H_2S until precipitation ceases, and filter. Dilute a portion of the filtrate small portion, dilute and treat the entire filtrate with H_2S until upon further with hot water.

Filtrate (1).—Reject.

Filtrate (2). Division B, Group I.—Set aside for treatment.

Filtrate (3).—Evaporate to dryness, add H_2SO_4, heat until fumes of H_2SO_4 appear, allow the acid to cool, and dilute it with three times its volume of water, transfer to a test-tube, filter, and wash with dilute H_2SO_4 (1:3).

Filtrate (4).—Add NH_4OH in excess and filter.

Filtrate (5).—Blue solution indicates *Cu.* If no color is visible, divide the solution. (*a*) Acidify with $HC_2H_3O_2$, and add $K_4FeC_6N_6$. P. mahogany-brown $Cu_2FeC_6N_6$ indicates *Cu.* (*b*) Warm, add HCl in *faint* excess, pass H_2S, filter, wash with hot water, transfer to a test-tube, boil in dilute H_2SO_4 (1:5), and filter. Dilute the filtrate with an equal volume of water, cool, and pass H_2S. P. yellow **CdS** indicates *Cd.*

(*c*) *Alternative of* (*b*).—Add KCN until blue color disappears. Pass H_2S and filter. P. yellow **CdS** indicates *Cd.*

SEPARATION AND IDENTIFICATION OF

Acidify the filtrate from Division A with HCl, filter, and wash.

Precipitate (1). DIVISION B.—SnS_2, Sb_2S_5, As_2S_5. Transfer to a test-tube with 5 cm.^{3} of water, add an equal volume of strong HCl, and warm without boiling for a few minutes. Allow to cool, pass H_2S, filter, and wash with HCl (1:1), and then thoroughy with water.

Residue (2).—Yellow As_2S_5 indicates *As.*

To confirm the presence of arsenic, dissolve a portion of the washed As_2S in HNO_3, boil until red fumes are no longer evolved, dilute and filter, divide: (*a*) To one portion add $AgNO_3$, and neutralize carefully with NH_4OH. P. brick-red Ag_3AsO_4 indicates *As*; (*b*) Add a few drops to about 5 cm.^{3} of the reagent solution of $(NH_4)_2MoO_4$ in dilute HNO_3, and warm. P. yellowish $(NH_4)_3AsO_4.11MoO_3.6H_2O$ indicates *As.*

As an alternative test for As treat the precipitate with a little strong HCl and a very little $KClO_3$, and divide the solution: (*a*) treat with Zn and HCl in a small Marsh's apparatus, and test the mirror with NaOCl; (*b*) treat with NH_4OH in excess and add magnesia mixture. P. white, crystalline NH_4MgAsO_4 confirms *As.*

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* A portion of the filtrate may be set aside and tested directly for *Sn* by

BASIC IONS OF GROUP II. DIVISION B.

Filtrate (1).—Reject.

* *Filtrate* (2).

Add oxalic acid (about 1 grm. to 10 cm.^{3} of the solution), warm, and add HCl if necessary to clear the solution. Pass H_2S.

Precipitate (3).	*Filtrate* (3).
Orange **Sb_2S_3** or **Sb_2S_5** indicates *Sb*. Should a dark coloration occur at this point, indicating **CuS** in traces, previously dissolved in the treatment by $(NH_4)_2S+S$, the precipitate should be treated with Na_2S, which dissolves the Sb_2S_5, leaving the **CuS**. After filtering, the residue may be tested for copper, and the filtrate acidified to precipitate the orange **Sb_2S_5**.	Boil to expel H_2S, add a little finely divided Zn and HCl, and warm until the Zn has disappeared. Filter, and to the filtrate add $HgCl_2$. P. white **Hg_2Cl_2** or gray or dark **Hg_2Cl_2+Hg** indicates *Sn*.

the Zn and HCl method of Filtrate (3) if *Sb* was found to be absent.

TABULAR VIEW OF GROUP II. DIVISION A.

Typical Salts.	Treatment with H_2S.	Treatment of P (1) with $(NH_4)_2S+S$.		Treatment of R (2) with HNO_3.		Treatment of F (3) with H_2SO_4.		Treatment of F (4) with NH_4OH.	
	P (1)	R (2)	F (2)	R (3)	F (3)	P (4)	F (4)	P (5)	F (5)
$HgCl_2$	**HgS**	**HgS**		**HgS**		......		......	
$PbCl_2$	**PbS**	**PbS**			$Pb(NO_3)_2$	**$PbSO_4$**		......	
$BiCl_3$	**Bi_2S_3**	**Bi_2S_3**			$Bi(NO_3)_3$		$Bi_2(SO_4)_3$	**$BiO(OH)$**	
$CuCl_2$	**CuS**	**CuS**			$Cu(NO_3)_2$		$CuSO_4$		$Cu(OH)_2$
$CdCl_2$	**CdS**	**CdS**			$Cd(NO_3)_2$		$CdSO_4$		$Cd(OH)_2$
H_3AsO_3	**As_2S_3**		$(NH_4)_3AsS_4$	......		......		......	
$SbCl_3$	**Sb_2S_3**		$(NH_4)_3SbS_4$	......		......		......	
$SnCl_2$	**SnS**		$(NH_4)_2SnS_3$	......		......		......	

TABULAR VIEW OF GROUP II. DIVISION B.

Filtrate from Div. A.	Treatment with HCl.		Treatment of P (1) with HCl (1:1) hot.	
	P (1)	F (1)	R (2)	F (2)
$(NH_4)_3AsS_4$	As_2S_5		As_2S_5	
$(NH_4)_3SbS_4$	Sb_2S_5			$SbCl_5$
$(NH_4)_2SnS_3$	SnS_2			$SnCl_4$

COMMENTARY UPON GROUP II.

The solution containing members of the group is acidified with hydrochloric acid before passing hydrogen sulphide, because in neutral or alkaline solution the precipitation of the sulphides of arsenic and antimony would not be complete.

Dilution with water before passing hydrogen sulphide often causes the precipitation of oxychlorides of antimony and bismuth, but if precipitated it is not necessary to redissolve them in hydrochloric acid, because they are readily changed to sulphides by the addition of hydrogen sulphide.

A large excess of hydrochloric acid is to be avoided on account of its solvent action, notably upon cadmium sulphide and tin sulphides; but this effect of the hydrochloric acid is obviated by diluting the filtrate with water after the first precipitation by hydrogen sulphide and treating repeatedly with hydrogen sulphide.

The color of the precipitated sulphides depends upon the relative amounts of the individual sulphides present. Mercuric sulphide, lead sulphide, bismuth sulphide, copper sulphide, and stannous sulphide are black or brownish black; cadmium sulphide, arsenious sulphide, arsenic sulphide, and stannic sulphide are yellow; and antimonious sulphide and antimonic sulphide are orange. Mercuric salts often give at first a white precipitate of a mercuric chlorosulphide, a double salt which on further treatment with hydrogen sulphide changes to black mercuric sulphide. Lead salts in the presence of considerable hydrochloric acid give with hydrogen sulphide a red lead chlorosulphide, which in excess of hydrogen sulphide is converted to the black lead sulphide.

Should arsenic be present in the higher condition of valence, its sulphide is very slowly precipitated, and is best formed at a temperature near that of boiling water.

Separation of Divisions A and B.

The division of the group depends upon the action of ammonium polysulphide upon the sulphides of arsenic, antimony, and tin in forming soluble sulpho-salts. The polysulphide is used because the excess of sulphur is necessary to the formation of the soluble ammonium sulpho-stannate, should tin be present as the stannous sulphide. The excess of sulphur in the ammonium polysulphide forms the sulpho-salts of the higher condition of valence with both antimony and arsenic, as well as with tin.

Copper sulphide may be to some extent attacked by ammonium polysulphide, and so may appear in traces with Division B. Its separation from the sulphides of Division B will be considered later.

The double salts which tend to form when hydrogen sulphide acts in limited amount upon mercuric and lead salts are converted by ammonium polysulphide as well as by an excess of hydrogen sulphide into simple sulphides.

The sulphides are warmed *gently* with ammonium polysulphide, because the cold reagent is slower in its action, while too high a temperature tends to cause not only a greater solvent action upon the cupric sulphide but also decomposition of the polysulphide itself.

After the treatment with the polysulphide, the residue, composed of the insoluble sulphides of Division A, should be thoroughly washed with water, to effect the complete removal of the soluble sulpho-salts of Division B.

Separation of the Members of Division A.

The separation of mercury from the other members of Division A depends upon the insolubility of mercuric sulphide in dilute nitric acid (1:3). It is important that the sulphides receive a thorough treatment with the acid, and that the dilute acid used be fully as strong as the mixture containing one part of acid in four parts of the water solution. Should the acid be more dilute, some of the other sulphides, particularly cupric sulphide, will not be acted upon and will remain with the mercuric sulphide. Strong nitric acid has some solvent action upon mercuric sulphide, and also tends to oxidize the lead sulphide almost entirely to lead sulphate, and it is therefore avoided.

The residue after the nitric acid treatment must always be tested for mercury. The presence of a black residue is not proof of the presence of mercury, because in the decomposition of the sulphides by nitric acid sulphur generally is a product, and it is often blackened by traces of cupric sulphide, lead sulphide, and bismuth sulphide enclosed in it. A white or yellow residue is not proof of the absence of mercury, because the action of nitric acid upon mercuric sulphide often yields a white compound of the composition $x\mathrm{Hg(NO_3)_2} \cdot y\mathrm{HgS}$, or a yellow mixture of this compound with sulphur. By the action of aqua regia upon the insoluble mercury residue mercuric chloride and mercuric nitrate are formed, which, when treated after dilution of the solution with stannous chloride, give white mercurous chloride, or a black mixture of mercurous chloride and mercury.

The separation of lead from bismuth, copper, and cadmium depends upon the formation of an insoluble sulphate when sulphuric acid is added to a solution containing salts of these ions. The nitric acid solution of the sulphides is evaporated to the fuming-point of the sulphuric acid in order to remove the more volatile nitric acid, in which lead sulphate is slightly soluble. The solution is diluted so that it may be filtered upon paper, and washed with dilute sulphuric acid, because the lead sulphate is more insoluble in dilute sulphuric acid than in water. The tendency of bismuth salts to become hydrolyzed, forming basic compounds in presence of water, is also overcome by the sulphuric acid used in removing the lead sulphate. The presence of lead may be readily confirmed by decomposing the sulphate either with ammonium acetate or with sodium hydroxide, and testing with potassium chromate in acetic acid solution.

The separation of bismuth from copper and cadimum depends upon the formation of insoluble bismuth hydroxide, while the hydroxides of copper and cadmium are soluble in excess of ammonium hydroxide. Traces of lead not completely separated as the sulphate may be precipitated with the bismuth as the hydroxide. The presence of bismuth may be confirmed by taking advantage of the characteristic behavior of bismuth salts when acted upon by large volumes of water, *i.e.*, the formation by hydrolysis of insoluble basic salts. In making the confirmatory test it is important to avoid the use of any considerable excess of hydrochloric acid in dissolving the bismuth hydroxide, because of the tendency of the acid to reverse the action by which the basic salt is formed.

The presence of a moderate amount of copper may be detected in the filtrate from the bismuth hydroxide by the blue color of the solution containing the copper-ammonium salt. Should copper be present in very small amounts a more delicate test for it is made by acidifying the ammoniacal solution with acetic acid and adding potassium ferrocyanide. A mahogany-brown precipitate of cupric ferrocyanide indicates copper.

The separation of copper from cadmium depends upon the solubility of the cadmium sulphide and the insolubility of the cupric sulphide in dilute sulphuric acid (1:5). Before the cadmium sulphide and the copper sulphide are precipitated by hydrogen sulphide the solution is acidified with hydrochloric acid, care being taken to avoid a large excess of the acid, because such excess prevents the precipitation of the cadmium sulphide. The precipitation of the cadmium sulphide can be assured by sufficiently diluting the filtrate and treating again with hydrogen sulphide. The alternative method for the separation of copper and cadmium needs no special comment further than to emphasize precautions in regard to the use of the *very poisonous* potassium cyanide.

Separation of the Members of Division B.

The filtrate obtained after the treatment of the sulphide of this group with ammonium polysulphide contains the sulpho-salts of arsenic, antimony, and tin in the higher condition of valence, and when these salts are decomposed by hydrochloric acid the higher sulphides are obtained. The formation of a precipitate when hydrochloric acid is added to acidity does not prove the presence of members of this division, because separation of a yellowish white precipitate of sulphur always takes place when ammonium polysulphide is acted upon by an acid. It is important to avoid an excess of hydrochloric acid over the amount necessary to acidify the solution, because of its solvent action upon stannic sulphide and antimonic sulphide. The color of the precipitate at this point gives some indication of the sulphides present, orange indicating antimonic sulphide, yellow arsenic sulphide or stannic sulphide, and brown traces of members of Division A (*e.g.*, cupric sulphide), present by reason of some slight action of ammonium polysulphide upon the sulphides of Division A.

5-7

The separation of arsenic from antimony and tin depends upon the action of hydrochloric acid upon antimonic sulphide and stannic sulphide, soluble chlorides being formed. The hydrochloric acid is warmed, not boiled, because boiling hydrochloric acid tends to cause loss of arsenic by formation of the volatile trichloride. The hydrogen sulphide is passed again before filtering, to reprecipitate any arsenic sulphide which may have dissolved. If the hydrochloric acid is not more dilute than 1:1 by volume, hydrogen sulphide will not reprecipitate the stannic sulphide and antimonic sulphide, and cold acid solutions of this strength may be filtered on good filter-paper. The hydrochloric acid (1:1) is first used rather than water in washing the arsenic sulphide to avoid the precipitation of sulphides of antimony and tin. The thorough washing of the arsenic sulphide with water before acting upon it with nitric acid preparatory to the test with silver nitrate is important, because of the interfering action of hydrochloric acid in any test involving the use of a soluble silver salt. The oxidation with nitric acid involves a long and thorough boiling, for upon the complete oxidation of arsenic sulphide to arsenic acid depends the satisfactory character of the silver nitrate and molybdate tests.

In the alternative test for arsenic with the Marsh apparatus the poisonous nature of the arsenic hydride should be borne in mind, and the test made under a good draught-hood. It is also important to remember that the air must be expelled from the apparatus before attempting to ignite the hydrogen. As arsenic is often an impurity in zinc, a blank test should be made on the metal used before employing it in the final test for arsenic. In (*b*) of the alternative test the necessity of the complete oxidation to arsenic acid should be borne in mind, and also the fact that the precipitation of ammonium-magnesium arsenate is started by rubbing the sides of the test-tube with a glass rod.

The separation of antimony and tin depends upon the fact that oxalic acid will prevent the precipitation of stannic sulphide by hydrogen sulphide, while antimonic sulphide is precipitated. If cupric sulphide was acted upon by ammonium polysulphide, it will appear with the antimonic sulphide as a dark coloration, and may be separated from it by sodium sulphide, which dissolves the antimonic sulphide.

In the test for tin the solution of stannic chloride is treated with zinc and hydrochloric acid to reduce the tin to the stannous condition. The action is continued until the metal disappears, in order to secure the solution of tin deposited upon the zinc in the course of the action. The test with the mercuric chloride should be made promptly upon the disappearance of the metal, in order that reoxidation of the stannous salt may not take place.

Important Reactions.

$HgCl_2 + H_2S = \mathbf{HgS} + 2HCl.$
$\mathbf{HgS} + 2O_2 + 2HCl = H_2SO_4 + HgCl_2.$*
$3HgCl_2 + 2SnCl_2 = \mathbf{Hg_2Cl_2} + \mathbf{Hg} + 2SnCl_4.$

$Pb(NO_3)_2 + H_2S = \mathbf{PbS} + 2HNO_3.$
$\mathbf{PbS} + 2HNO_3 = Pb(NO_3)_2 + H_2S.$
$Pb(NO_3)_2 + H_2SO_4 = \mathbf{PbSO_4} + 2HNO_3.$
$\mathbf{PbSO_4} + 2NH_4C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4.$

$2BiCl_3 + 3H_2S = \mathbf{Bi_2S_3} + 6HCl.$
$\mathbf{Bi_2S_3} + 6HNO_3 = 2Bi(NO_3)_3 + 3H_2S.$
$2Bi(NO_3)_3 + 3H_2SO_4 = Bi_2(SO_4)_3 + 6HNO_3.$
$Bi_2(SO_4)_3 + 6NH_4OH = \mathbf{2BiO(OH)} + 3(NH_4)_2SO_4 + 2H_2O.$
$\mathbf{BiO(OH)} + 3HCl = BiCl_3 + 2H_2O.$
$BiCl_3 + H_2O = \mathbf{BiOCl} + 2HCl.$

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* Typical.

$CuCl_2 + H_2S = \mathbf{CuS} + 2HCl$.
$\mathbf{CuS} + 2HNO_3 = Cu(NO_3)_2 + H_2S$.
$Cu(NO_3)_2 + H_2SO_4 = CuSO_4 + 2HNO_3$.
$CuSO_4 + 4NH_4OH = CuSO_4.4NH_3.H_2O$* $+ 3H_2O$.
$2Cu(C_2H_3O_2)_2 + K_4FeC_6N_6 = \mathbf{Cu_2FeC_6N_6} + 4K\cancel{Cl}$. Ac

$CdCl_2 + H_2S = \mathbf{CdS} + 2HCl$.
$\mathbf{CdS} + 2HNO_3 = Cd(NO_3)_2 + H_2S$.
$Cd(NO_3)_2 + H_2SO_4 = CdSO_4 + 2HNO_3$.
$\mathbf{CdS} + H_2SO_4 = CdSO_4 + H_2S$.

$2H_3AsO_3 + 3H_2S = 6H_2O + \mathbf{As_2S_3}$.
$\mathbf{As_2S_3} + 3[(NH_4)_2S + S] = 2(NH_4)_3AsS_4 + S_2$.†
$2(NH_4)_3AsS_4 + 6HCl = 3H_2S + \mathbf{As_2S_5} + 6NH_4Cl$.
$\mathbf{As_2S_5} + 10O_2 + 8H_2O = 2H_3AsO_4 + 5H_2SO_4$.
$H_3AsO_4 + 3AgNO_3 + 3NH_4OH = \mathbf{Ag_3AsO_4} + 3H_2O + 3NH_4NO_3$.
$H_3AsO_4 + MgCl_2 + NH_4Cl + 3NH_4OH$
$= \mathbf{MgNH_4AsO_4} + 3H_2O + 3NH_4Cl$.
$H_3AsO_4 + 8H = 4H_2O + AsH_3$.
$4AsH_3 + 3O_2 = 6H_2O + \mathbf{As}$.
$2\mathbf{As} + 3NaOCl = 3NaCl + As_2O_3$.

$2SbCl_3 + 3H_2S = \mathbf{Sb_2S_3} + 6HCl$.
$2\mathbf{Sb_2S_3} + 3[(NH_4)_2S + S] = 2(NH_4)_3SbS_4 + S_2$.
$2(NH_4)_3SbS_4 + 6HCl = 6NH_4Cl + \mathbf{Sb_2S_5} + 3H_2S$.
$\mathbf{Sb_2S_5} + 10HCl = 2SbCl_5 + 5H_2S$.

$SnCl_2 + H_2S = \mathbf{SnS} + 2HCl$.
$\mathbf{SnS} + (NH_4)_2S + S = (NH_4)_2SnS_3$.
$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2S + \mathbf{SnS_2}$.
$\mathbf{SnS_2} + 4HCl = SnCl_4 + 2H_2S$.
$SnCl_4 + Zn = ZnCl_2 + SnCl_2$.
$SnCl_2 + 2HgCl_2 = SnCl_4 + \mathbf{Hg_2Cl_2}$.

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* Typical. † Forming a soluble higher ammonium polysulphide.

CHARACTERISTIC REACTIONS OF BASIC IONS.

GROUP III.

TYPICAL COMPOUND.	$AlCl_3$	$CrCl_3$	$FeCl_3$
REAGENT. $NaOH$	P. white AlO_3H_3. Sol. in excess as $NaAlO_2$. Reprecipitated by NH_4Cl.	P. green CrO_3H_3. Sol. in excess. Reprecipitated on boiling.	P. reddish brown FeO_3H_3. Insol. in excess.
NH_4OH	P. white AlO_3H_3. Slightly sol. in excess. Ammonium salts tend to increase insolubility.	P. green CrO_3H_3. Slightly sol. in excess to solution of pinkish color. Tends to precipitate on boiling.	P. reddish brown FeO_3H_3. Insol. in excess.
Na_2CO_3 or $(NH_4)_2CO_3$	P. white, basic salt essentially AlO_3H_3. Slightly sol. in excess.	P. green basic salt essentially CrO_3H_3. Somewhat sol. in excess.	P. reddish brown basic salt essentially FeO_3H_3.
$NaC_2H_3O_2 + HC_2H_3O_2$ —not more than 4%.	P. on boiling, white basic acetate approximating more or less to AlO_3H_3.	P. on boiling, green basic acetate. Precipitates best in presence of basic ferric acetate.	P. on boiling, reddish brown basic acetate.
$(NH_4)_2S$	P. white AlO_3H_3.	P. green CrO_3H_3.	P. black FeS. Sol. in acids to *ferrous* salts.
H_2S	....	....	Reduction to $FeCl_2$ with separation of sulphur.

CHARACTERISTIC REACTIONS OF BASIC IONS.

GROUP III (*Concluded*).

TYPICAL COMPOUND.	$AlCl_3$	$CrCl_3$	$FeCl_3$
REAGENT.			
Na_2HPO_4	P. white. $AlPO_4$ (normal) or of form less acid than $H_6Al(PO_4)_3$ Sol. in HCl. " NaOH.	P. green. $CrPO_4$ (normal) or of form less acid than $H_6Cr(PO_4)_3$. Sol. in HCl. Decomposed by NaOH.	P. yellowish white. $FePO_4$ (normal) or of form less acid than $H_6Fe(PO_4)_3$. Sol. in HCl. Decomposed by NaOH.
$K_3FeC_6N_6$	....	....	Brown or dark-green color.
$K_4FeC_6N_6$	P. white or *none* at all.	....	P. dark blue $Fe_4Fe_3C_{18}N_{18}$. Insol. in HCl. Decomposed by NaOH.
$KClO_3+Na_2CO_3$ in fusion or $KClO_3+HNO_3$ on boiling.	....	Forms yellow soluble chromate or chromic acid.	....
$KSCN$	....	....	Blood-red color. $FeS_3C_3N_3$, most delicate with HCl.
Borax bead (oxidizing and reducing flames).	O. F. .... R. F.	{ Yellowish green, hot. Emerald-green, cold. { Yellowish green, hot. Emerald-green, cold.	{ Red, hot. Yellow, cold. { Green, hot. Green, cold.

SEPARATION AND IDENTIFICATION OF BASIC IONS OF GROUP III.

The solution containing members of this group should be tested for the presence of ferric salts before the regular analysis of the group is begun. Take a few drops of the solution to be tested, dilute with water, add HCl, divide, and make the following tests :

(*a*) Add $K_4FeC_6N_6$.—Blue P. or coloration $Fe_4Fe_3C_{18}N_{18}$ indicates Fe^{III}.

* (*b*) Add KSCN.—Red coloration $FeS_3C_3N_3$ indicates Fe^{III}.

A. Hydroxide Method.

Add NH_4OH to alkaline reaction and boil until the odor of ammonia is faint, filter and wash.

Precipitate (1).—Hydroxides of *Al, Cr, Fe.* Dissolve in strong HNO_3 (as little as possible), add cautiously a few crystals of $KClO_3$, and boil. The color indicates the degree of oxidation of the chromium, if much is present. Dilute, add NaOH in excess, and filter.

Filtrate (1). Reject.

Precipitate (2).—Reddish FeO_3H_3. [The presence or absence of the iron is determined in the tests described above.]

Filtrate (2).—Divide. (1) Acidify with HCl, add NH_4OH to faint alkalinity, and boil; or add NH_4Cl in quantity sufficient to destroy the excess of NaOH, and boil until the odor of NH_3 is faint. P. white, flocky AlO_3H_3 indicates *Al.* (2) Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$. P. yellow $PbCrO_4$ indicates *Cr.*

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* This test should be made in the absence of nitrogen oxides.

B. Basic Acetate Method.

Neutralize the cold solution by $(NH_4)_2CO_3$ to incipient precipitation. If the precipitate is not red in color, dissolve in dilute HCl, add ferric chloride until the red ferric hydroxide falls when $(NH_4)_2CO_3$ is added. Redissolve the precipitate in the least possible amount of HCl. Add an excess of $NH_4C_2H_3O_2$ (perhaps 2 grm.), dilute abundantly, and boil. Filter hot, and wash with hot water.

Precipitate (1).—Basic acetates of *Al, Cr, Fe.*
(*a*) Treat according to the Hydroxide Method, Precipitate (1).
(*b*) Or dissolve the precipitate in HCl, add NaOH in excess, and filter.

Filtrate (1).
Reject.

Precipitate (2).
Reddish FeO_3H_3.

Filtrate (2).—Divide. (1) Test for *Al* as in the Hydroxide Method, Filtrate (2). (2) Add H_2O_2 or Na_2O_2 until there is no further change of green to yellow, add $Pb(C_2H_3O_2)_2$ in solution and $HC_2H_3O_2$ to acidity. P. yellow **$PbCrO_4$** indicates *Cr.*

TABULAR VIEW OF GROUP III.

	A.			B.		
Typical Salts.	Treatment with NH_4OH and boiling.	Treatment of P (1) with HNO_3+KClO_3 and NaOH in excess.		Treatment with $(NH_4)C_2H_3O_2$ and boiling.	Treatment of P (1) with HCl and NaOH in excess.	
	P (1)	P (2)	F (2)	P (1)	P (2)	F (2)
$AlCl_3$	$Al(OH)_3$		$NaAlO_2$	*$Al(OH)(C_2H_3O_2)_2$		$NaAlO_2$
$FeCl_3$	$Fe(OH)_3$	$Fe(OH)_3$		*$Fe(OH)(C_2H_3O_2)_2$	$Fe(OH)_3$	
$CrCl_3$	$Cr(OH)_3$		Na_2CrO_4	*$Cr(OH)(C_2H_3O_2)_2$		$NaCrO_2$

* Typical.

COMMENTARY UPON GROUP III.

The solution containing members of this group is tested first for the presence of iron. In making these tests it is well to bear in mind their extreme delicacy, and to use small amounts of the solution. Nitric acid and oxides of nitrogen must be absent when the sulphocyanide test is made, on account of their interfering action. The presence of a small amount of hydrochloric acid increases the delicacy of these tests.

A. In the separation of this group by ammonium hydroxide the solution is boiled to remove the excess of ammonium hydroxide, because of the slight solvent action of that reagent in excess upon the hydroxides of aluminium and chromium.

In the oxidation process potassium chlorate is added cautiously to prevent explosive decomposition of large amounts of chloric acid. The oxidation of the chromium is indicated by the change from green to yellow or red, unless the amount of iron salt present is large enough so that its color masks the chromium colors.

The sodium hydroxide is added in excess not only to insure the complete separation of the ferric hydroxide, but to redissolve the aluminium hydroxide first formed, and to form the soluble sodium aluminate.

In the first test for aluminium the hydrochloric acid must be used to acid reaction to change the aluminate to aluminium chloride, and after the addition of ammonium hydroxide to alkalinity the solution must be boiled to remove any large excess of that reagent. In the second test for aluminium it is important to remember that a considerable amount of ammonium chloride is generally necessary to destroy the excess of sodium hydroxide, according to the equation $NH_4Cl+NaOH=NaCl+NH_3+H_2O$. For this reason the addition of ammonium chloride and the boiling should be continued until but slight odor of ammonia is apparent.

In the test for chromium care must be taken to have the solution acid with acetic acid before the addition of the lead salt, so that lead hydroxide may not be precipitated.

B. The alternative or acetate process requires more time in the manipulation, but has the advantage of overcoming any tendency of the basic ions of following groups to form insoluble hydroxides, thus accomplishing a more satisfactory separation of this group from the groups that follow. Moreover, if phosphates are present the phosphoric acid ion is removed as ferric phosphate, which is insoluble, while under the conditions of the acetate precipitation in the presence of acetic acid, phosphates of the basic ions of the following groups do not appear.

The solution is neutralized to incipient precipitation with ammonium carbonate to remove excess of the more active acids. The addition of ferric chloride until red ferric hydroxide falls when ammonium carbonate is added, is to insure the presence of enough of the ferric ion to combine with the phosphoric acid ion if present, and to assist in the precipitation of the basic acetates, as the basic acetates of aluminium and chromium form more readily if ferric acetate is formed at the same time. The ammonium acetate used must be made as nearly neutral as possible, since excess of ammonium hydroxide would precipitate hydroxides instead of basic acetates, and great excess of acetic acid would prevent the partial hydrolysis of the acetates, that is, the formation of basic acetates.

Care must be taken to avoid the use of an excess of hydrochloric acid in redissolving the hydroxides, because upon the addition of the acetate acetic acid is formed, and this, if considerable in amount, is disadvantageous, as has been shown. The water is added in large volume (*e.g.*, 300–400 cm.^{3}) and the solution boiled, because large dilution and high temperature are most favorable conditions to the hydrolysis of the acetates with formation of the insoluble basic acetates. The basic acetates are filtered hot and washed with hot water to prevent the reversion of the partial hydrolysis and the conversion of the basic acetates to soluble salts. Sodium chromite, formed by the action of sodium hydroxide upon chromic hydroxide, is oxidized to sodium chromate by hydrogen peroxide or sodium peroxide.

Should phosphoric acid be present with this group it may appear as white lead phosphate when lead acetate is added to the solution containing the chromate. This white precipitate does not however mask the yellow color of the chromate.

Important Reactions.

$4FeCl_3 + 3K_4FeC_6N_6 = \mathbf{Fe_4(FeC_6N_6)_3} + 12KCl.$
$FeCl_3 + 3KSCN = Fe(SCN)_3 + 3KCl.$
$FeCl_3 + 3NH_4OH = \mathbf{Fe(OH)_3} + 3NH_4Cl.$
$Fe(NO_3)_3 + 3NaOH = \mathbf{Fe(OH)_3} + 3NaNO_3.$
$FeCl_3 + 3NH_4C_2H_3O_2 = Fe(C_2H_3O_2)_3 + 3NH_4Cl.$
$Fe(C_2H_3O_2)_3 + H_2O = \mathbf{Fe(OH)(C_2H_3O_2)_2} + HC_2H_3O_2.$

$AlCl_3 + 3NH_4OH = \mathbf{Al(OH)_3} + 3NH_4Cl.$
$Al(NO_3)_3 + 4NaOH = 3NaNO_3 + NaAlO_2 + 2H_2O.$
$NaAlO_2 + 4HCl = AlCl_3 + NaCl + 2H_2O.$
$NaAlO_2 + NH_4Cl + H_2O = NaCl + NH_3 + \mathbf{Al(OH)_3}.$
$AlCl_3 + 3NH_4C_2H_3O_2 = Al(C_2H_3O_2)_3 + 3NH_4Cl.$
$Al(C_2H_3O_2)_3 + H_2O = \mathbf{Al(OH)(C_2H_3O_2)_2} + HC_2H_3O_2.$

$CrCl_3 + 3NH_4OH = \mathbf{Cr(OH)_3} + 3NH_4Cl.$
$2Cr(OH)_3 + O_3$ (from $HNO_3 + KClO_3$) $= 2H_2CrO_4 + H_2O.$
$H_2CrO_4 + 2NaOH = Na_2CrO_4 + 2H_2O.$
$Na_2CrO_4 + Pb(C_2H_3O_2)_2 = \mathbf{PbCrO_4} + 2NaC_2H_3O_2.$
$CrCl_3 + 4NaOH = 3NaCl + NaCrO_2 + 2H_2O.$
$2NaCrO_2 + 3Na_2O_2 + H_2O = 2Na_2CrO_4 + 2NaOH.$

CHARACTERISTIC REACTIONS

GROUP

TYPICAL COMPOUND.	*Fe*Cl_2	*Co*Cl_2
REAGENT.		
*Na*OH	P. white FeO_2H_2. Oxidizes rapidly becoming greenish and finally reddish brown. FeO_3H_3 is the final product. Insol. in excess. Pure *unoxidized* FeO_2H_2 is sol. in NH_4Cl and acids.	P. blue, basic salt (on boiling pink) CoO_2H_2. Oxidizes becoming brownish. CoO_3H_3 is the final product. Insol. in excess. *Pure* CoO_2H_2 is sol. in NH_4Cl, NH_4OH and in acids.
NH$_4$OH	P. white FeO_2H_2 rapidly becoming green. In presence of NH_4Cl is not precipitated but the solution oxidizes and throws down reddish brown FeO_3H_3.	P. basic salt. Sol. in excess to reddish solution. In presence of NH_4Cl not thrown down.
Na$_2$CO$_3$	P. white $FeCO_3$ slightly sol. in NH_4Cl. Oxidizes rapidly.	P. pink $CoCO_3$ (basic). Sol. in NH_4Cl and NH_4OH.
(*NH*$_4$)$_2$CO$_3$	P. white $FeCO_3$. Sol. in excess. Oxidizes rapidly.	P. pink $CoCO_3$ (basic). Sol. in excess.
(*NH*$_4$)$_2$S	P. black FeS. Sol. in HCl. Sol. in $HC_2H_3O_2$. Oxidizes easily.	P. black CoS. Insol. in very dil. HCl. Insol. in $HC_2H_3O_2$. Sol. in aqua regia.

OF BASIC IONS.

IV.

$NiCl_2$	$MnCl_2$	$ZnCl_2$
P. apple-green NiO_2H_2. Oxidizes becoming brown. NiO_3H_3 is the final product. Insol. in excess. *Pure* NiO_2H_2 sol. in NH_4Cl, NH_4OH and in acids.	P. white MnO_2H_2. Oxidizes becoming brown. $Mn_2O_4H_2$ is the final product. Oxidized to $HMnO_4$ by PbO_2 + HNO_3. Insol. in excess. Sol. in NH_4Cl and in acids.	P. white ZnO_2H_2. Sol. in excess. " NH_4OH. " NH_4Cl. " acids.
P. apple-green NiO_2H_2. Sol. in excess to bluish solution. In presence of NH_4Cl not thrown down.	P. partial, white MnO_2H_2. Sol. in NH_4Cl. In presence of NH_4Cl, dark-brown product of oxidation.	P. white ZnO_2H_2. Sol. in excess. In presence of NH_4Cl not thrown down.
P. green $NiCO_3$ (basic). Sol. in NH_4Cl and NH_4OH.	P. nearly white $MnCO_3$. Slightly sol. in NH_4Cl but excess of precipitant tends to prevent solution.	P. white $ZnCO_3$ (basic). Sol. in NH_4Cl. " NH_4OH. " NaOH.
P. green $NiCO_3$ (basic). Sol. in excess.	P. nearly white $MnCO_3$. Insol. in excess. Slightly sol. in presence of NH_4Cl.	P. white $ZnCO_3$ (basic). Sol. in excess.
P. black NiS. Insol. in very dil. HCl. Insol. in $HC_2H_3O_2$. Sol. in aqua regia.	P. flesh-colored* MnS. Sol. in HCl. Sol. in $HC_2H_3O_2$. Oxidizes easily.	P. white ZnS. Sol. in HCl. Insol. in $HC_2H_3O_2$.

* Sometimes greenish or gray,

CHARACTERISTIC REACTIONS

GROUP

TYPICAL COMPOUND.	$FeCl_2$	$CoCl_2$
REAGENT.		
H_2S	Ordinarily in acid solution no P. In $HC_2H_3O_2$ in presence of an alkali acetate, incomplete P. FeS. In neutral solution of salts of common acids, no P. or very little.	Ordinarily in acid solution no P. In very dil. $HC_2H_3O_2$ in presence of an alkali acetate, P. CoS. In neutral solution of salts of common acids, partial P.
$K_4FeC_6N_6$	P. bluish white $K_2Fe_2C_6N_6$ or $Fe_2FeC_6N_6$, changing to blue. Insol. in HCl.	P. green, becoming blue $Co_2FeC_6N_6$. Insol. in HCl.
$K_3FeC_6N_6$	P. dark blue $Fe_3Fe_2C_{12}N_{12}$. Insol. in HCl. [Decomposed by alkali hydroxides.]	P. dark brown $Co_3Fe_2C_{12}N_1$ Insol. in HCl. Insol. in NH_4OH
Borax bead	O. F. $\left\{\begin{array}{l}\text{red, hot.}\\ \text{yellow, cold.}\end{array}\right.$ R. F. $\left\{\begin{array}{l}\text{green, hot.}\\ \text{green, cold.}\end{array}\right.$	O. F. $\left\{\begin{array}{l}\text{blue.}\\ \text{blue.}\end{array}\right.$ R. F. $\left\{\begin{array}{l}\text{blue.}\\ \text{blue.}\end{array}\right.$
Bead of $Na_2CO_3+KNO_3$	Opaque, dark or dirty.	Opaque, dark or dirty

OF BASIC IONS.

IV (*Concluded*).

$Ni\mathrm{Cl}_2$	$Mn\mathrm{Cl}_2$	$Zn\mathrm{Cl}_2$
Ordinarily in acid solution no P. In *very* dil. $HC_2H_3O_2$ in presence of an alkali acetate P. **NiS.** In neutral solution of salts of common acids partial P.	In acid solution no P. even in dilute $HC_2H_3O_2$ in presence of an alkali acetate. In neutral solution of salts of common acids little or no P.	Ordinarily in acid solution (except $HC_2H_3O_2$) no P. In $HC_2H_3O_2$, P. **ZnS.** In neutral solution of salts of common acids partial P.
P. greenish white $Ni_2FeC_6N_6$. Insol. in HCl.	P. nearly white $Mn_2FeC_6N_6$. Sol. in HCl.	P. white $Zn_2FeC_6N_6$. Somewhat sol. in HCl.
P. yellowish green $Ni_3Fe_2C_{12}N_{12}$. Insol. in HCl. Sol. in NH_4OH.	P. brown $Mn_3Fe_2C_{12}N_{12}$. Insol. in HCl.	P. yellowish brown $Zn_3Fe_2C_{12}N_{12}$. Sol. in HCl.
O. F. $\begin{cases}\text{violet.}\\ \text{red-brown.}\end{cases}$ R. F. $\begin{cases}\text{gray and turbid.}\\ \text{gray and turbid.}\end{cases}$	O. F. $\begin{cases}\text{violet-red.}\\ \text{amethystine.}\end{cases}$ R. F. $\begin{cases}\text{colorless.}\\ \text{colorless.}\end{cases}$	O. F. $\begin{cases}\text{colorless.}\\ \text{colorless.}\end{cases}$ R. F. $\begin{cases}\text{colorless.}\\ \text{colorless.}\end{cases}$
Opaque, dark or dirty.	Opaque, characteristic green.	Opaque, white.

SEPARATION AND IDENTIFICATION OF

Take a few drops of the solution containing members of this group, dilute
(*a*) Add $K_3FeC_6N_6$—Blue P. or coloration
(*b*) Add $K_4FeC_6N_6$—Blue P. or coloration
(*c*) Add KSCN—Red coloration (in the
The presence of iron in the ferrous condition having been indicated in the
warm until the iron is all in the ferric condition. Now separate the iron from
of Group III.

To the solution from which iron has been separated, add NH_4Cl and NH_4OH
wash with water containing H_2S.

Precipitate (1).
CoS, NiS, ZnS, MnS.
Acidify with $HC_2H_3O_2$ and filter.

Residue (2).
CoS, NiS, ZnS.
Wash with hot water, dissolve in the least possible
amount of aqua regia, boil, cool, add NaOH in excess,
filter, and wash.*

Precipitate (3).
$Co(OH)_2$, $Ni(OH)_2$
Divide and treat according to
Ferricyanide and Cobaltinitrite Methods,
given on page 54.

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* If the filtrate is blue, too much NaOH was used. Acidify, there-

† If the indication is doubtful, filter, and burn the paper moistened

BASIC IONS OF GROUP IV.

with water, add HCl, divide, and test as follows:
$Fe_3Fe_2C_{12}N_{12}$ indicates *Fe*^{II}.
$Fe_4Fe_3C_{18}N_{18}$ indicates *Fe*^{III}.
absence of oxides of nitrogen) $FeS_3C_3N_3$ indicates *Fe*^{III}.
preliminary tests, treat the remainder of the solution with a little HNO_3, the
other members of this group by the Hydroxide Method or Basic AcetateMethod

to alkalinity, if necessary. Warm, pass H_2S to complete precipitation, and

Filtrate (1).
Reject.

Filtrate (2).
$Mn(C_2H_3O_2)_2$.
Add NH_4OH in faint excess and pass H_2S.

Precipitate (4).
P. flesh-colored **MnS** indicates *Mn*. Confirm (1) by the bead of $Na_2CO_3+KNO_3$. Robin's-egg blue. (2) By PbO_2 and HNO_3. (Boil with HNO_3, add PbO_2, warm, and allow to settle.) Purple color.

Filtrate (4).
Reject.

Filtrate (3).
Add $HC_2H_3O_2$ in faint excess and divide. (1) Pass H_2S. P. white **ZnS** indicates *Zn*.† (2) Add $K_4FeC_6N_6$. P. white **$Zn_2FeC_6N_6$** indicates *Zn*.

fore, again with HCl, add NaOH in excess to recover dissolved cobalt.
with a drop of $Co(NO_3)_2$ on Pt. foil. Green ash indicates *Zn*.

A. FERRICYANIDE METHOD.

Dissolve the hydroxides in $HC_2H_3O_2$, add a little aluminium salt in solution, and $K_3FeC_6N_6$ in distinct excess. Add NH_4OH in excess.

Precipitate.	*Filtrate.*
$Co_3(FeC_6N_6)_2$ Rose color indicates *Co.*	To about 5 cm.^{3} add a piece of solid KOH or NaOH about the size of a pea, and warm gently. P. black **$Ni(OH)_3$** indicates *Ni.*

B. COBALTINITRITE METHOD.

Test a portion by the borax bead. A blue bead indicates *Co.* If the bead shows no blue color, but is violet or red-brown in the oxidizing flame, and gray and turbid in the reducing flame, *Ni* is indicated. If Co is indicated, or if the mass of NiO_2H_2 is so great as to mask the presence of a little Co, dissolve the remainder of the precipitate in HCl, evaporate off any great excess of acid, add Na_2CO_3 in faint excess, then KNO_2 in excess followed by $HC_2H_3O_2$ in faint excess, taking care to keep the volume of the liquid small (5–10 cm.^{3}). Warm gently, set aside for 24 hours, and then filter.

Precipitate.	*Filtrate.*
Yellow **$K_3Co(NO_2)_6.xH_2O$** indicates *Co.* Confirm by the borax bead.	Add more KNO_2, keeping the solution acid with $HC_2H_3O_2$, and set aside for some hours. If further precipitation occurs, filter, add to the filtrate, or to the solution in which no further precipitation took place, NaOH in excess. P. apple-green **NiO_2H_2** indicates *Ni.* Confirm by borax bead.

TABULAR VIEW OF GROUP IV.

Typical Salts.	Treatment with H_2S in ammoniacal solution and addition of $HC_2H_3O_2$.		Treatment of P (1) with aqua regia and NaOH in excess.		A Treatment of P (3) with $HC_2H_3O_2$, $K_3FeC_6N_6$, and NH_4OH.		B Treatment of P (2) with HCl, Na_2CO_3, KNO_2, $HC_2H_3O_2$.	
	R (2)	F (2)	P (3)	F (3)	P	F	P	F
$Ni(C_2H_3O_2)_2$	**NiS**		**$Ni(OH)_2$**		**$Co_3(FeC_6N_6)_2$**			$Ni_2(C_2H_3O_2)_2$
$Co(C_2H_3O_2)_2$	**CoS**		**$Co(OH)_2$**				**$K_3Co(NO_2)_6.xH_2O$**	
$Zn(C_2H_3O_2)_2$	**ZnS**			Na_2ZnO_2		**$Ni(OH)_2$** sol.	....	
$Mn(C_2H_3O_2)_2$		$Mn(C_2H_3O_2)_2$	....		....		....	

COMMENTARY UPON GROUP IV.

Iron in the ferrous condition, Fe^{II}, falls naturally in this group. Inasmuch, however, as ferrous salts change to the ferric condition when exposed to the action of air, a ferrous salt is ordinarily associated with some ferric salt. For this reason, and to facilitate the separation as well, it is best in beginning the analysis of Group IV first to test for the presence of iron, then to convert to the ferric condition all iron present in the ferrous condition, and finally to remove the iron by the hydroxide method or the basic acetate method of Group III, before proceeding further with the analysis of the group.

The members of Group IV give insoluble sulphides with hydrogen sulphide in ammoniacal solution. Before adding ammonium hydroxide care is taken to insure a sufficient amount of ammonium salt to prevent the precipitation of the hydroxides.

The color of the precipitate may give some indication of the members present. Cobalt sulphide and nickel sulphide are black, zinc sulphide is white, and manganese sulphide is generally pink.

The sulphides should be completely precipitated before acetic acid is added, because nickel sulphide and cobalt sulphide are often not completely thrown down in the presence of that acid, although when once precipitated they are unaffected by it. After the addition of acetic acid to dissolve the manganese sulphide, the residue should be washed with hydrogen sulphide water to prevent its oxidation to soluble sulphates. When the filtrate from the acetic acid treatment is made alkaline with ammonium hydroxide there is generally enough hydrogen sulphide present to cause a partial precipitation of the manganese sulphide. It can be completely thrown down by the addition of more hydrogen sulphide.

The color of the manganese sulphide depends upon the conditions under which the precipitation was made. It is generally pink, but may be greenish or gray. The presence of manganese is easily confirmed by the sodium carbonate bead test, should the color of the sulphide give doubtful indication.

The mixed sulphides of cobalt, nickel, and zinc are decomposed by aqua regia, and the solution of the chlorides thus formed is treated with sodium hydroxide in excess. Here, again, as in the previous group, care must be taken in adding the hydroxide to the strongly acid solution.

As the separation of the zinc from the cobalt and nickel depends upon the formation of a sodium zincate by excess of sodium hydroxide upon the zinc hydroxide first formed, a sufficient excess of the hydroxide must be present or zinc will be left with the cobalt and nickel. Too great an excess of the sodium hydroxide is shown by the formation of a soluble blue cobalt compound.

In the detection of zinc by ferrocyanide the complete decomposition of the zincate by neutralization of the free alkali with acetic acid is important, on account of the decomposing action of sodium hydroxide upon the ferrocyanides. Care should be observed in the addition of potassium ferrocyanide, so that the solution may not become yellow and disguise the white zinc ferrocyanide. In the confirmation of the zinc sulphide by the cobalt nitrate test it is important to use a very dilute solution of the nitrate, on account of the dark color which a large excess of cobaltic oxide gives to the ash, and which masks the green color.

The residue left after the removal of the zinc by the excess of sodium hydroxide contains cobalt and nickel hydroxides. This precipitate may be divided, the greater part being treated by the first method, *A*, and the remainder by the alternative method, *B*, for the separation of cobalt and nickel.

A. The cobalt may be detected by the borax bead if the amount of nickel present is not so much in excess of the cobalt as to mask the blue color of the bead. Should this, however, be the case, the precipitate of the mixed hydroxides of cobalt and nickel is dissolved in the smallest possible amount of dilute hydrochloric acid, the free hydrochloric acid destroyed by the addition of sodium carbonate to incipient precipitation, and the solution cleared by the careful addition of acetic acid. By this method the more active hydrochloric acid is replaced by the less active acetic acid, which is less likely to decompose the potassium cobaltinitrite to be formed. The volume of the liquid is kept small, because when it is large potassium cobaltinitrite is appreciably soluble. An excess of the potassium nitrite is necessary, not only for the formation of the complex salt but also for the oxidation of the cobalt to the cobaltic condition. Potassium nitrite often contains from its manufacture some excess of free alkali. Care must therefore be taken to have the solution acid with acetic acid before setting aside for the complete precipitation of the double salt, lest nickel hydroxide be precipitated with the cobalt salt.

B. In the alternative or ferricyanide method, the addition of the aluminium salt is to aid in the filtration of the cobalt ferricyanide, which otherwise is filtered with difficulty on account of its finely divided character. The presence of the gelatinous aluminium hydroxide makes the retention of the cobalt salt on the filter easily possible. The potassium ferricyanide is best added in solid form, because of the desirability of keeping the volume of the liquid small. Special care should be taken to insure an excess of the potassium ferricyanide, both to bring about a complete precipitation of the cobalt and nickel ferricyanides, and to effect the oxidation of the nickel later. The ammonium hydroxide should be added slowly, with agitation of the liquid, because of the possibility of some solvent action upon the cobalt salt. Should the filtrate from the treatment with ammonium hydroxide have a reddish tinge, indicating such a solvent action, it should be acidified with acetic acid, and the process of separation repeated.

The test for nickel by this process is so delicate that 0.1 mg. may be found in 5 cm.^{3} of the ammoniacal filtrate. As the oxidation takes place best in concentrated solution, the potassium hydroxide is added in solid form.

Important Reactions.

$CoCl_2+H_2S+2NH_4OH=\mathbf{CoS}+2NH_4Cl+2H_2O.$

$\mathbf{CoS}+2O_2+2HCl=CoCl_2+H_2SO_4.$

$CoCl_2+2NaOH=\mathbf{Co(OH)_2}+2NaCl.$

$$2Co(C_2H_3O_2)_2+2KNO_2+4HC_2H_3O_2=2Co(C_2H_3O_2)_3 \\ +2KC_2H_3O_2+2H_2O+2NO.$$

$$Co(C_2H_3O_2)_3+6KNO_2+xH_2O=\mathbf{Co(NO_2)_3.3KNO_2.}x\mathbf{H_2O} \\ +3KC_2H_3O_2.$$

$3Co(C_2H_3O_2)_2+2K_3FeC_6N_6=\mathbf{Co_3(FeC_6N_6)_2}+6KC_2H_3O_2.$

$NiCl_2+H_2S+2NH_4OH=\mathbf{NiS}+2NH_4Cl+2H_2O.$

$\mathbf{NiS}+2O_2+2HCl=NiCl_2+\cancel{2}H_2SO_4.$

$NiCl_2+NaOH=\mathbf{Ni(OH)_2}+2NaCl.$

$3Ni(C_2H_3O_2)_2+2K_3FeC_6N_6=\mathbf{Ni_3(FeC_6N_6)_2}+6KC_2H_3O_2.$

$\mathbf{Ni(OH)_2}+KOH+K_3FeC_6N_6=\mathbf{Ni(OH)_3}+K_4FeC_6N_6.$

$MnCl_2 + H_2S + 2NH_4OH = \mathbf{MnS} + 2H_2O + 2NH_4Cl.$

$\mathbf{MnS} + 2HC_2H_3O_2 = Mn(C_2H_3O_2)_2 + 2H_2S.$

$\mathbf{MnS} + 2Na_2CO_3 + 3O_2 = Na_2MnO_4 + Na_2SO_4 + 2CO_2.$

$$\left\{\begin{array}{l} 2\mathbf{MnS} + 8HNO_3 = 2MnSO_4 + 4N_2O_3 + 4H_2O. \\ 2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad + 3Pb(NO_3)_2 + 2H_2O. \end{array}\right.$$

$ZnCl_2 + H_2S + 2NH_4OH = \mathbf{ZnS} + 2H_2O + 2NH_4Cl.$

$\mathbf{ZnS} + 2O_2 + 2HCl = ZnCl_2 + H_2SO_4.$

$ZnCl_2 + 4NaOH = Na_2ZnO_2 + 2NaCl + 2H_2O.$

$Na_2ZnO_2 + 4HC_2H_3O_2 = 2NaC_2H_3O_2 + Zn(C_2H_3O_2)_2 + 2H_2O.$

$Zn(C_2H_3O_2)_2 + H_2S = \mathbf{ZnS} + HC_2H_3O_2.$

$2Zn(C_2H_3O_2)_2 + K_4FeC_6N_6 = \mathbf{Zn_2FeC_6N_6}.$

CHARACTERISTIC REACTIONS OF BASIC IONS.

GROUP V.

TYPICAL COMPOUND.	$Ba(NO_3)_2$	$Sr(NO_3)_2$	$Ca(NO_3)_2$
REAGENT. $NaOH$	P. white BaO_2H_2, only in concentrated solutions. Sol. in acids.	P. white SrO_2H_2, only in concentrated solutions. Sol. in acids.	P. white CaO_2H_2, sparingly sol. Sol. in acids.
NH_4OH	....	....	....
Na_2CO_3	P. white $BaCO_3$. Sol. in acids.	P. white $SrCO_3$. Sol. in acids.	P. white $CaCO_3$. Sol. in acids.
$(NH_4)_2CO_3$	P. white $BaCO_3$. Sol. in acids.	P. white $SrCO_3$. Sol. in acids.	P. white $CaCO_3$. Sol. in acids.
$(NH_4)_2C_2O_4$	P. white BaC_2O_4. Sol. in HCl. Slightly sol. in $HC_2H_3O_2$.	P. white SrC_2O_4. Sol. in HCl. Slightly sol. in $HC_2H_3O_2$.	P. white CaC_2O_4. Sol. in HCl. Almost insol. in $HC_2H_3O_2$.
H_2SO_4	P. white $BaSO_4$. Insol. in acids except concentrated H_2SO_4.	P. white $SrSO_4$. Very little sol. in H_2O or dilute acids.	P. white $CaSO_4$ in concentrated solutions. Sparingly sol. in H_2O, especially on boiling.

CHARACTERISTIC REACTIONS OF BASIC IONS.

GROUP V (*Concluded*).

TYPICAL COMPOUND.	$Ba(NO_3)_2$	$Sr(NO_3)_2$	$Ca(NO_3)_2$
REAGENT. K_2CrO_4	P. yellow **$BaCrO_4$**. Insol. in dilute $HC_2H_3O_2$ when an excess of K_2CrO_4 has been used.	Sol. except in concentrated solution.	....
Na_2HPO_4	P. white **$HBaPO_4$**. Practically insol.	P. white **$HSrPO_4$**. Practically insol.	P. white **$HCaPO_4$**. Practically insol.
Na_2HPO_4 NH_4OH	P. white **$Ba_3(PO_4)_2$**. Sol. in acids. Somewhat sol. in NH_4Cl.	P. white **$Sr_3(PO_4)_2$**. Sol. in acids. Somewhat sol. in NH_4Cl.	P. white **$Ca_3(PO_4)_2$**. Sol. in acids. Somewhat sol. in NH_4Cl.
Dehydration in amyl alcohol.	P. white **$Ba(NO_3)_2$**.	P. white **$Sr(NO_3)_2$**.	No deposit or very little appearing as a slight spot which on ignition and retreatment dissolves.
Flame test.	Yellow-green.	Crimson.	Orange-red.
Spectroscope test.	Spectrum complex. Characteristic,— 4 *green* lines.	Spectrum complex. Characteristic,— 2 *red* lines. 1 *orange* line. 1 *blue* line.	Spectrum complex. Characteristic,— 1 *green* line. 1 *orange* line.

SEPARATION AND IDENTIFICATION OF

To the solution containing members of this group, add NH_4OH to alkaline $(NH_4)_2CO_3$ volatilized, and filter.

Precipitate (1).—**$BaCO_3$, $SrCO_3$, $CaCO_3$.** Wash, dissolve in as little $HC_2H_3O_2$ as possible, add K_2CrO_4.

Precipitate (2).—Yellow **$BaCrO_4$** indicates *Ba.*

Precipitate (3).—**$SrCO_3$, $CaCO_3$.** Wash carefully, dissolve (not more than 0.2 grm.) in HNO_3, evaporate nearly to dryness, add 5 cm.³ of amyl alcohol, dehydrate thoroughly by boiling until the temperature rises to the normal boiling-point of the alcohol, or until escaping fumes burn with a dense flame at the mouth of the tube, taking care that the volume of the alcohol shall not decrease below 5 cm.³ If no residue is left, *Sr* is absent. If a deposit forms, it indicates *Sr* or a *trace* of *Ca.* Filter the liquid through a small dry filter.

Residue (4).—If the indication is doubtful rinse the tube and adherent deposit with 5 cm.³ of absolute ethyl alcohol, ignite the residue gently, redissolve in a drop of HNO_3, evaporate nearly to dryness, and again dehydrate with 5 cm.³ of amyl alcohol. The formation of deposit, **$Sr(NO_3)_2$**, indicates *Sr.*

BASIC IONS OF GROUP V.

reaction, and $(NH_4)_2CO_3$. Boil a few minutes, taking care to replace the

***Filtrate* (1).**
Reject.

***Filtrate* (2).—Make alkaline with NH_4OH, add $(NH_4)_2CO_3$, heat to boiling, and filter.**

***Filtrate* (3).**
Reject.

***Filtrate* (4).—Add an equal volume of ethyl alcohol and a little dilute H_2SO_4. Faint cloudiness settling on long standing may be due to *Sr*, but a floating, flocky, $CaSO_4$, indicates *Ca*.**

TABULAR VIEW OF GROUP V.

Typical Salts.	Treatment with $(NH_4)_2CO_3$ and boiling.		Treatment of P (1) with $HC_2H_3O_2$ and K_2CrO_4.		Treatment of F (2) with $(NH_4)_2CO_3$.	Treatment of P (3) with HNO_3 and $C_5H_{11}OH$.	
	P (1)	F (1)	P (2)	F (2)	P (3)	R (4)	F (4)
$BaCl_2$	$BaCO_3$		$BaCrO_4$		....	....	
$SrCl_2$	$SrCO_3$			$Sr(C_2H_3O_2)_2$	$SrCO_3$	$Sr(NO_3)_2$	
$CaCl_2$	$CaCO_3$			$Ca(C_2H_3O_2)_2$	$CaCO_3$		$Ca(NO_3)_2$

COMMENTARY UPON GROUP V.

The solution containing members of this group is made alkaline with ammonium hydroxide, to prevent the possibility of setting free carbon dioxide and forming soluble acid carbonates upon addition of the ammonium carbonate, and to inhibit the dissociation of the excess of ammonium carbonate on boiling.

The carbonates are dissolved in acetic acid rather than in a more active acid, because in a moderate amount of that acid the barium chromate is not decomposed. In precipitating the barium chromate the solution should not be too concentrated, on account of the danger of precipitating some strontium chromate also. The carbonates of strontium and calcium, after reprecipitation, must be very thoroughly washed to remove all traces of soluble salts. The special reason for this precaution is that these alkali salts become insoluble in the amyl alcohol to be used in testing for the strontium.

The carbonates of strontium and calcium should be decomposed in the very smallest possible amount of dilute nitric acid; indeed, if the amount of the carbonates is large, it would be advantageous to leave some undissolved, in order to avoid the presence of any excess of nitric acid, which tends to decompose the alcohol on evaporation. Should an excess of nitric acid be present with the nitrates, it must be removed as fully as possible by evaporation before adding the alcohol. In the separation of strontium from calcium, amyl alcohol is preferred to absolute ethyl alcohol or to a mixture of absolute ethyl alcohol and ether, because its boiling-point, 128°–130°, is so high that dehydration may be brought about by boiling. The difficult problem of completely drying the nitrates before treatment is thus avoided.

The ignition of the fumes of the alcohol is recommended, in order to avoid their disagreeable odor and to prevent large amounts of the heavy vapor from collecting about the tube and igniting suddenly. Then, too, the point at which the complete dehydration of the salts has taken place can be fairly well determined by noticing when the fumes burn quietly, the burning being intermittent so long as water-vapor is mixed with the fumes. Not more than 0.2 grm. of the nitrates should be present, because that is about the limit of the solubility of calcium nitrate in 5 $cm.^3$ of amyl alcohol. In the process of dehydration one must use care to keep the volume from decreasing below 5 $cm.^3$, on account of the resulting separation of the calcium nitrate from lack of solvent.

If the conditions stated have been carefully observed, a distinct separation of salt on dehydration indicates the presence of strontium. If the deposit should be very slight, so as to make the test seem doubtful, it would be well to pour off the alcohol, rinse this deposit with absolute ethyl alcohol, ignite it in the tube, dissolve in a drop of dilute nitric acid, and repeat the process of dehydration. It has sometimes been found that such slight deposits as described result when no strontium is present. This is probably due to the formation either of a calcium salt of some organic acid or of basic calcium nitrate. In any case it is always possible to get it into solution by the treatment described. The use of the dry filter in separating the strontium deposit is to avoid the solvent action of water upon such particles of the strontium nitrate as may come in contact with the paper.

Such solvent action would, of course, vitiate the test for calcium to be made upon the filtrate.

The addition of the ethyl alcohol to the amyl alcohol filtrate is to obtain a liquid with which the dilute sulphuric acid will mix freely. The extremely slight solubility of strontium in amyl alcohol (5 cm.^{3} of the alcohol will dissolve about 0.3 mg. of strontium nitrate) is frequently the occasion of the formation of a slight, finely granular precipitate of strontium sulphate in the filtrate from the alcohol treatment when the sulphuric acid is added. The calcium sulphate, however, precipitated under these conditions, takes on a flocky form, and generally floats in the alcoholic solution, and is thus distinguished from strontium sulphate. A considerable precipitation is, of course, conclusive evidence of the presence of calcium. In case of doubt, the application of the spectroscope to the detection of strontium and calcium is always helpful.

Important Reactions.

$BaCl_2 + (NH_4)_2CO_3 = \mathbf{BaCO_3} + 2NH_4Cl$.
$\mathbf{BaCO_3} + 2HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + H_2O + CO_2$.
$Ba(C_2H_3O_2)_2 + K_2CrO_4 = \mathbf{BaCrO_4} + 2KC_2H_3O_2$.

$SrCl_2 + (NH_4)_2CO_3 = \mathbf{SrCO_3} + 2NH_4Cl$.
$\mathbf{SrCO_3} + 2HC_2H_3O_2 = Sr(C_2H_3O_2)_2 + CO_2 + H_2O$.
$\mathbf{SrCO_3} + 2HNO_3 = Sr(NO_3)_2 + CO_2 + H_2O$.

$CaCl_2 + (NH_4)_2CO_3 = \mathbf{CaCO_3} + 2NH_4Cl$.
$\mathbf{CaCO_3} + 2HC_2H_3O_2 = Ca(C_2H_3O_2)_2 + CO_2 + H_2O$.
$\mathbf{CaCO_3} + 2HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O$.
$Ca(NO_3)_2 + H_2SO_4 = \mathbf{CaSO_4} + 2HNO_3$.

CHARACTERISTIC REACTIONS

GROUP

TYPICAL COMPOUND.	$MgCl_2$	$NaCl$	$LiCl$
REAGENT.			
KOH or $NaOH$	P. white MgO_2H_2 Sol. in acids. Sol. in NH_4Cl.	....	....
NH_4OH	P. white MgO_2H_2 partial only.	....	....
Na_2CO_3	P. white $xMgCO_3.yMgO_2H_2$.	....	P. white Li_2CO_3 in cold concentrated solution.
Na_2HPO_4	P. white $HMgPO_4$ with NH_4OH. NH_4MgPO_4 crystalline.	....	P. white Li_3PO_4 sparingly sol. NH_4 salts prevent precipitation except on boiling.
KH_2AsO_4 $+NH_4OH$	P. white crystalline NH_4MgAsO_4.	....	....
$Na_3Co(NO_2)_6$	....	....	....
Flame	....	Yellow.	Red.
Spectrum	....	Yellow line.	Carmine line.

OF BASIC IONS.

VI.

$K\mathrm{Cl}$	$NH_4\mathrm{Cl}$	TYPICAL COMPOUND.
		REAGENT.
....	Free $\mathrm{NH_3}$ on boiling.	$K\mathrm{OH}$ or $Na\mathrm{OH}$
....	....	$NH_4\mathrm{OH}$
....	Free $\mathrm{NH_3}$ on boiling.	$Na_2\mathrm{CO_3}$
....	....	$Na_2H\mathrm{PO_4}$
....	....	$KH_2\mathrm{AsO_4}$ $+NH_4\mathrm{OH}$
P. yellow $\mathrm{K_3Co(NO_2)_6}$. Insol. in dilute acetic acid.	P. yellow $\mathrm{(NH_4)_3Co(NO_2)_6}$ Insol. in dilute acetic acid.	$Na_3\mathrm{Co(NO_2)_6}$.
Violet.	....	Flame
Red line.	....	Spectrum

SEPARATION AND IDENTIFICATION OF

(*a*) To a small portion of the solution containing members of this group
upon moistened red litmus paper, turning it blue, indicate *NH_4*.

(*b*) To the remainder of the solution add NH_4OH to alkalinity and an
warm.

Precipitate (1).
White cryst. **NH_4MgAsO_4** indicates *Mg*.

Precipitate (2).
As_2S_3.

BASIC IONS OF GROUP VI.

add solid $Ca(OH)_2$ and warm. Odor of ammonia and action of the fumes

ammoniacal solution of $(NH_4)_3AsO_4$ cautiously, to complete precipitation, and

Filtrate (1).

Acidify with HCl, add H_2SO_3, boil out excess of SO_2, and pass H_2S.

Filtrate (2).

Evaporate to dryness. Ignite to remove NH_4 salts, dissolve in a few drops of water and a drop of dilute HCl, and filter if necessary. Divide.

(*a*) Add Na_2CO_3 to alkalinity, $HC_2H_3O_2$ to acidity, and $Na_3Co(NO_2)_6$ and warm. Yellow $K_3Co(NO_2)_6$ indicates *K*.

(*b*) Evaporate to a few drops and test before the spectroscope.

Yellow line indicates *Na*.
Red line indicates *K*.
Crimson line indicates *Li*.

TABULAR VIEW OF GROUP VI.

Typical Salts.	Treatment with $NH_4OH + (NH_4)_3AsO_4$.		Treatment in HCl with H_2SO_3 and H_2S.	
$MgCl_2$	NH_4MgAsO_4		As_2S_3	
KCl		KCl		KCl
NaCl		NaCl		NaCl
LiCl		LiCl		LiCl
		$(NH_4)_3AsO_4$		

COMMENTARY UPON GROUP VI.

The test for ammonium salts is made at the beginning of the analysis of this group, because ammonium salts are used later as reagents.

In the treatment with calcium hydroxide it is important to avoid any spattering of the solution upon the litmus paper, as this would turn the red paper blue. Moistened litmus paper is more sensitive than dry.

It is important that solutions in which the magnesium is to be precipitated be made ammoniacal, but not too strongly ammoniacal, and warmed in order to secure a crystalline condition of the precipitated ammonium-magnesium arsenate. It is advisable to avoid unnecessary excess of the arsenate, because arsenic must be removed by hydrogen sulphide before testing for the alkali elements.

The filtrate from the magnesium arsenate is acidified and boiled with sulphur dioxide to reduce the arsenic to the arsenious condition, in which it is more readily precipitated as the sulphide than in the higher condition of oxidation.

The ammonium salts are removed before the potassium cobaltinitrite test for potassium is made, because these salts give an insoluble ammonium cobaltinitrite similar to the potassium salt. The presence of the ammonium salts would interfere also with the spectroscopic test, since they tend to cool the flame and protect the alkali salts from dissociation in the flame.

Before making the spectroscopic tests it is advantageous to concentrate the solutions to be tested.

Important Reactions.

$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$

$MgCl_2 + (NH_4)_3AsO_4 = 2NH_4Cl + \mathbf{MgNH_4AsO_4}.$

$3KC_2H_3O_2 + Co(NO_2)_3.3NaNO_2$
$= \mathbf{Co(NO_2)_3.3KNO_2} + 3NaC_2H_3O_2.$

GROUP SEPARATIONS IN

I. Test a small portion of the original solution for the presence and con-
under Group VI.

II. To about 10 cm.^{3} of the solution to be analyzed add a few drops o

Precipitate (1), *Group* I.

Wash with dilute HCl, and proceed as indicated in the treatment of Precipitate (1) in the analysis of Group I.

Precipitate (2), *Group* II.

Proceed as indicated in the treatment of Precipitate (1) in the analysis of Group II.

THE BASIC ANALYSIS.

dition of oxidation of Fe as directed under Group IV, and for NH_4 as directed

dilute HCl.

Filtrate (1), *Groups* II–VI.

Dilute to about 100 cm.^{3} If precipitation takes place on dilution add HCl to clear the solution. Warm, pass H_2S to complete precipitation.

Filtrate (2), *Groups* III–VI.

Boil to expel H_2S. Divide. (*a*) Take about 10 cm.^{3}; evaporate to dryness and desiccate at 110° C. Of the residue ignite a small portion—carbonization indicating carbonizing organic matter. Treat the remainder with a little HCl and then with hot water and filter.

Residue.

Test in a bead of $NaPO_3$. An insoluble residue indicates SiO_2.

Filtrate.

Add $BaCl_2$ to complete precipitation and filter. Add Na_2CO_3 in distinct excess to the filtrate and filter. To the filtrate now obtained add $HC_2H_3O_2$ in slight excess and then $CaCl_2$. P. white CaC_2O_4 indicates C_2O_4.

(*b*) Treat the remainder of Filtrate (2) according to the indications of (*a*):

I. If carbonizing organic matter or oxalic acid has been indicated, evaporated to dryness, fuse with NH_4NO_3, treat the residue with dilute HCl (and if silica has been indicated evaporate to dryness and desiccate at 110° C. and extract again with dilute HCl), and filter if there is any residue.

II. If neither carbonizing organic matter nor oxalic acid has been indicated warm with HNO_3 to oxidize Fe^{II} previously reduced by H_2S. If solution is not complete, filter.

Residue (1).—Wash, fuse with Na_2CO_3 in platinum, extract with water, filter.

Residue (2).—Wash, dissolve in HCl, and test for members of Group V.

Filtrate.—Reject.

Filtrate (2)

(*Continued on p. 77*).

Precipitate (3), *Group* III. Proceed as indicated in the treatment of Precipitate (1), Group III, 2.

Precipitate (4). CoS, NiS, ZnS

Precipitate (5). MnS.

Precipitate (6), *Group* V.—Proceed as indicated in the treatment of Group V.

Filtrate (2) (*Continued*).

After the removal of Residue (1) by filtration, divide the filtrate. (*a*) To a small portion add NH_4Cl, if not already present in sufficient amount, NH_4OH in faint excess, and boil. P. is AlO_3H_3, CrO_3H_3, FeO_3H_3, or phosphates of Groups III, IV, or V. (*b*) If no precipitate was found by NH_4OH, pass at once to Group IV. If a precipitate was found by NH_4OH, take care to insure the sufficient presence of NH_4Cl. Neutralize the cold solution by $(NH_4)_2CO_3$ to incipient precipitation. If the precipitate is not red in color, redissolve in dilute HCl, add ferric chloride until the red ferric hydrate falls when $(NH_4)_2CO_3$ is added. Redissolve the precipitate in the least possible amount of HCl. Add an excess of $NH_4C_2H_3O_2$ (perhaps 2 grm.), dilute abundantly, and boil. Filter hot, and wash with hot water.

Filtrate (3), *Groups* IV–VI.

Add NH_4Cl if necessary. Add NH_4OH to alkaline reaction, and pass H_2S. *Group* IV is now insoluble, with *Groups* V and VI in solution. Acidify with $HC_2H_3O_2$ and filter.

Filtrate (4), *Groups* V, VI, besides *Mn*.

Add NH_4 OH and pass H_2S.

Filtrate (5), *Groups* V, VI.

Acidify with HCl, concentrate to 5 cm.^{3} Add about 5 cm.^{3} of aqua regia and evaporate to dryness to remove excess of (NH_4) salts. Dissolve in water and a little dilute HCl. Add NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$ and boil. Filter and wash.

Filtrate (6), *Group* VI. Proceed as indicated in the treatment of Group VI.

TABULAR VIEW OF GROUP SEPARATIONS IN THE BASIC ANALYSIS.

Typical Salts. X = Cl or NO_3.	Treatment with HCl.		Treatment with H_2S.		Acetate treatment after boiling out H_2S and oxidizing with HNO_3.		Treatment with H_2S in ammoniacal solution and acidification with acetic acid.		Treatment with NH_4OH.		Treatment with NH_4OH + $(NH_4)_2CO_3$.		Treatment with $(NH_4)_3AsO_4$.	
	P (1)	F (1)	P (2)	F (2)	P (3)	F (3)	P (4)	F (4)	P (5)	F (5)	P (6)	F (6)	P (7)	F (7)
AgX	AgCl													
Hg_2X_2	Hg_2Cl_2													
PbX_2	$PbCl_2$	PbX_2	PbS			X = Cl, NO_3, or $C_2H_3O_2$								
HgX_2		HgX_2	HgS											
BiX_3		BiX_3	Bi_2S_3					X = Cl, NO_3, or $C_2H_3O_2$		X = Cl, NO_3, or $C_2H_3O_2$				
CuX_2		CuX_2	CuS									X = Cl, NO_3, $C_2H_3O_2$, or $\frac{1}{2}CO_3$		X = Cl, NO_3, $C_2H_3O_2$, or $\frac{1}{2}CO_3$
CdX_2		CdX_2	CdS											
AsX_3		AsX_3	As_2S_3											
SbX_3		SbX_3	Sb_2S_3											
SnX_2		SnX_2	SnS											
AlX_3		AlX_3		AlX_3	$Al(OH)(C_2H_3O_2)_2$									
CrX_3		CrX_3		CrX_3	$Cr(OH)(C_2H_3O_2)_2$									
FeX_3		FeX_3	S	FeX_2	$Fe(OH)(C_2H_3O_2)_2$									
CoX_2		CoX_2		CoX_2		CoX_2	CoS							
NiX_2		NiX_2		NiX_2		NiX_2	NiS							
MnX_2		MnX_2		MnX_2		MnX_2		MnX_2	MnS					
ZnX_2		ZnX_2		ZnX_2		ZnX_2	ZnS							
BaX_2		BaX_2		BaX_2		BaX_2		BaX_2		BaX_2	$BaCO_3$			
SrX_2		SrX_2		SrX_2		SrX_2		SrX_2		SrX_2	$SrCO_3$			
CaX_2		CaX_2		CaX_2		CaX_2		CaX_2		CaX_2	$CaCO_3$			
MgX_2		MgX_2		MgX_2		MgX_2		MgX_2		MgX_2		MgX_2	NH_4MgAsO_4	
NaX		NaX		NaX		NaX		NaX		NaX		NaX		NaX
KX		KX		KX		KX		KX		KX		KX		KX
LiX		LiX		LiX		LiX		LiX		LiX		LiX		LiX
NH_4X		NH_4X		NH_4X		NH_4X		NH_4X		NH_4X		NH_4X		NH_4X

COMMENTARY UPON GROUP SEPARATIONS IN THE BASIC ANALYSIS.

In considering the basic analysis with reference to the possible presence of members of all the groups, certain special points in the group separations require consideration.

Preliminary Tests.—Preliminary tests are made for the presence and condition of iron salts and the presence of ammonium salts.

The iron tests are made upon the original solution, because that element changes its condition of oxidation from time to time during the course of the analysis. If iron is present originally in the ferrous condition, exposure to the oxygen of the air causes partial or even complete change to the ferric condition. This change is also readily brought about by the presence or addition of oxidizing agents, such as nitric acid, chlorine, etc. If the iron is originally in the ferric condition, hydrogen sulphide or other reducing agents will convert it to the ferrous condition.

Ammonium salts are tested for in the original solution, because the addition of ammonium hydroxide, chloride, carbonate, and acetate during the analysis makes later testing valueless.

Group I.—The addition of hydrochloric acid for the precipitation of the chlorides of Group I should be made with care to avoid unnecessary excess of the acid. A large excess of the acid not only may have a solvent action upon the chlorides precipitated, but tends later to prevent the complete precipitation of certain of the sulphides of Group II, especially cadmium sulphide. The oxychlorides of bismuth and antimony are sometimes precipitated when hydrochloric acid is added to a solution of the salts of those elements. If precipitated they will dissolve in excess of the acid. Some chlorides are insoluble in strong hydrochloric acid (*e.g.*, sodium chloride, potassium chloride, barium chloride), and will separate if strong hydrochloric acid is added in the separation of Group I. Such precipitation may be avoided by the use of dilute hydrochloric acid, or by working with dilute solutions.

After the separation of the chlorides of Group I by filtration, the first washing of the precipitate should be made with dilute hydrochloric acid, because of the possibility of leaving on the filter insoluble basic chlorides of antimony and bismuth, formed when water acts upon the soluble chlorides of those elements. If, upon addition of water to the filtrate from Group I, a precipitate separates, such separation is probably due to the formation of the above-mentioned insoluble basic salts.

Group II.—Hydrogen sulphide, being a reducing agent, acts upon ferric salts to change them to the ferrous condition, upon red chromic acid to form green chromic salts, and upon purple permanganic acid to form nearly colorless or pink manganous salts. All these processes of reduction are accompanied by corresponding oxidation of the hydrogen sulphide, with separation of sulphur and formation of sulphuric acid. Some precipitation of sulphur and formation of sulphuric acid may be brought about by nitric acid if present in sufficient amount. Such formation of sulphuric acid in a solution containing members of Group V (barium, strontium, calcium) may result in the inconvenient precipitation of insoluble sulphates of this group. If nitric acid is known to be present in the solution, it should therefore be removed so far as possible before the treatment with hydrogen sulphide. The possibility of the formation of sulphuric acid, through oxidation of the hydrogen sulphide by the oxygen of the air or by oxidizing agents, makes it advisable to examine, as indicated, for the members of Group V which may be present as sulphates, any insoluble material remaining after such oxidation may have taken place. As soon as the sulphides of Group II have been completely precipitated by hydrogen sulphide and removed by filtration, the filtrate should be boiled until the hydrogen sulphide is completely removed, in order to prevent its oxidation to sulphuric acid on standing in the air.

Group III.—Before beginning the analysis of Group III it is necessary to test for certain kinds of organic matter which interfere with the group precipitation. Of such interfering organic substances, tartaric acid and citric acid and their salts, which char on heating to a carbonaceous residue, are common examples. Oxalic acid and oxalates are the only common substances of this sort which do not char on heating. The test must be made, therefore, for organic matter which chars on heating, and for oxalic acid and oxalates, which do not char. In testing for organic matter by heating, it is important to distinguish between charring, or carbonization, and simple blackening, which may be due to the formation of some dark-colored oxide. In the test described for the oxalic ion the sodium carbonate should be added in distinct excess, to decompose the barium oxalate which tends to form when the solution is just neutralized; and in the final step of the test care should be taken to avoid a considerable excess of acetic acid, on account of its solvent action upon calcium oxalate.

Silicates are often present as the result of the action of solutions upon glass vessels used during the analysis, and the silicic ion is to be tested for and removed before beginning the analysis of Group III, because of the tendency of silicic acid to separate in a form resembling aluminium hydroxide when the tests for aluminium are being made. The removal of the silicic ion is effected by desiccating the residue left upon evaporating the solution after treatment with hydrochloric acid, the product being nearly anhydrous silicon dioxide.

The test for members of Group III by ammonium hydroxide is valuable, because, should no precipitation take place with that reagent, the entire examination for this group may be omitted.

Group IV.—After the removal of the members of Group III by the acetate process, the amount of ammonium salt in the filtrate is sufficient without further addition to prevent the precipitation of the hydroxides of Group IV when ammonium hydroxide is added.

Group V.—The filtrate from Group IV should not be allowed to stand, nor should nitric acid be added, without previous removal of hydrogen sulphide, on account of the possibility of the formation of sulphuric acid and the consequent precipitation of the members of Group V as sulphates.

The complete precipitation of the members of this group by ammonium carbonate may be materially interfered with by large amounts of ammonium salts accumulated in the previous analytical processes, such salts tending to reverse the reaction in which the insoluble carbonates are formed. In order to prevent this action of the large amount of ammonium salts, the filtrate from Group IV is evaporated to dryness with aqua regia, which decomposes the ammonium salts.

PART III.

THE ACIDIC ANALYSIS.

REACTIONS AND METHODS.

THE Acidic Analysis is that part of Qualitative Analysis which treats of the identification of the Negative or Acidic Ions.

CHARACTERISTIC REACTIONS OF ACIDIC IONS.

GROUP I.

REAGENT.	$BaCl_2$	$CaCl_2$	$AgNO_3$	$Pb(C_2H_3O_2)_2$	Special tests.
TYPICAL COMPOUND.					
Na_2SO_4	P. white **$BaSO_4$**. Insol. in HCl.	P. white **$CaSO_4$**. Except in dilute solutions. Sol. in acids. Somewhat sol. in H_2O.	P. white **Ag_2SO_4**. Only in concentrated solutions.	P. white **$PbSO_4$**. Sol. in NaOH. Sol. in ammonium acetate.	Heated on charcoal with Na_2CO_3 gives Na_2S, which when moistened and put upon a silver coin forms black **Ag_2S**.
Na_2SiF_6	P. white **$BaSiF_6$**. Insol. in HCl.	. . . .	. . . .	. . . .	Strong H_2SO_4 liberates SiF_4+2HF. The fumes acting on a moistened rod deposit **H_4SiO_4**.
Na_2SO_3	P. white **$BaSO_3$**. Sol. in HCl.	P. white **$CaSO_3$**. Sol. in HCl.	P. white **Ag_2SO_3**. Sol. in HNO_3. Decomposed by boiling into **Ag**.Ag_2SO_4,SO_2, turning gray.	P. white **$PbSO_3$**. Sol. in HNO_3.	Reduces $KMnO_4$ on acidifying. Bleaches iodine forming Na_2SO_4+2HI. Gives Na_2S on charcoal. Gives with acids odor of SO_2 ***without*** separating ***sulphur***.

*Na_2*S_2O_3	P. white **BaS_2O_3**. Only in concentrated solutions	....	P. white **$Ag_2S_2O_3$**. Sol. in HNO_3. Sol. in excess of thiosulphate. Decomposed on boiling into *black* **Ag_2S**+ H_2SO_4.	P. white **PbS_2O_3**. Decomposes on boiling into **PbS**+H_2SO_4.	Gives SO_2+S with HCl. On charcoal gives Na_2S. Acts as a solvent of AgCl. Bleaches iodine forming $Na_2S_4O_6$ which is oxidized to Na_2SO_4 by bromine.
*Na_2H*PO_4	P. white. Sol. in acids.	P. white. Sol. in acids (even in $HC_2H_3O_2$).	P. yellow **Ag_3PO_4**. Sol. in HNO_3. Sol. in NH_4OH.	P. white. Sol. in NaOH. Insol. in NH_4OH.	P. with Mg mixture, white NH_4MgPO_4. P. with MoO_3 mixture in excess (20:1) yellow **$(NH_4)_3PO_4.11MoO_3$. $6H_2O$.**
*KH_2*AsO_4	P. white in neutral solutions. Sol. in acids.	P. white. Sol. in acids (even in $HC_2H_3O_2$).	P. reddish brown **Ag_3AsO_4**. Sol. in HNO_3. Sol. in NH_4OH.	P. white. Sol. in HNO_3. Insol. in $HC_2H_3O_2$.	P. with Mg mixture, white **NH_4MgAsO_4**. P. with MoO_3 mixture in excess (20:1) yellow **$(NH_4)_3AsO_4.(MoO_3)_4$. $6H_2O$.**
*K_3*AsO_3	P. white. Sol. in acids.	P. white. Sol. in acids (even in $HC_2H_3O_2$).	P. yellow **Ag_3AsO_3**. Sol. in HNO_3. Sol. in NH_4OH.	P. white. Sol. in acids (even in $HC_2H_3O_2$).	

CHARACTERISTIC REACTIONS OF ACIDIC IONS.

GROUP I (*Concluded*).

REAGENT.	*Ba*Cl$_2$	*Ca*Cl$_2$	*Ag*NO$_3$	*Pb*(C$_2$H$_3$O$_2$)$_2$	Special tests.
TYPICAL COMPOUND.					
K$_2$CrO$_4$	P. yellow **BaCrO$_4$**. Sol. in HNO$_3$. Insol. in dil. HC$_2$H$_3$O$_2$.	....	P. purplish red **Ag$_2$CrO$_4$**. Sol. in HNO$_3$.	P. yellow **PbCrO$_4$**. Sol. in NaOH.	**Reduced to green CrCl$_3$ by boiling with HCl+ alcohol.**
Na$_2$B$_4$O$_7$	P. white. Difficultly sol. in H$_2$O. Sol. in acids.	P. white. Sol. in acids.	P. white. Sol. in HNO$_3$. Sol. in NH$_4$OH.	P. white. Sol. in excess of the lead salt.	**Moistened with H$_2$SO$_4$+ alcohol gives green flame. Made acid with HCl and put on turmeric-paper gives on drying at 100° pink color which touched with NaOH darkens to green or black.**
Na$_4$SiO$_4$	P. white.	P. white.	P. yellow, only in concentrated solution.	P. white.	**The separated SiO$_2$ heated in a bead of Na$_2$CO$_3$ evolves CO$_2$, and heated in a bead of NaPO$_3$ fails to dissolve and shows skeleton of SiO$_2$.**

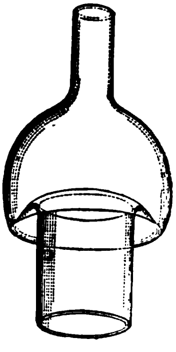
Na_2CO_3	P. white **$BaCO_3$**. Sol. in acids.	P. white **$CaCO_3$**. Sol. in acids.	P. gray Ag_2CO_3. Sol. in acids.	P. white **$PbCO_3$** (basic). Sol. in acids.	Acids liberate CO_2, found by action on lime-water or baryta-water.
NaF	P. white **BaF_2**. Sol. in HCl.	P. white **CaF_2**. Sol. in HCl. Insol. in $HC_2H_3O_2$.	....	P. white. Sol. in HNO_3.	H_2SO_4 liberates HF which etches glass. H_2SO_4 + a silicate liberates SiF_4, which acts on a moistened rod to deposit **H_4SiO_4**.
$Na_2C_2O_4$	P. white. Sol. in HCl or HNO_3.	P. white. Sol. in HCl or HNO_3. Insol. in $HC_2H_3O_2$.	P. white. Sol. in HNO_3.	P. white. Sol. in HNO_3.	Yields CO_2+CO with strong H_2SO_4. With strong $H_2SO_4+MnO_2$ evolves CO_2. Decolorizes $KMnO_4$ in hot acid solution.
$Na_2C_4H_4O_6$	P. white. Sol. in HCl. " NH_4Cl.	P. white. Sol. in NaOH, reprecipitated on boiling. Quite sol. in NH_4Cl. Sol. in HCl.	P. white (in case of alkali salts). Sol. in HNO_3. " NH_4OH. Solution gives a mirror of silver on warming.	P. white. Sol. in NaOH.	Formation of difficultly soluble acid salts of K or NH_4 by acids. Bleaching action on $KMnO_4$. Formation of mirror.

IDENTIFICATION OF ACIDIC IONS OF GROUP I.

[1] Acidify with HCl a portion of the solution contained in a test-tube.*

Evolution of Gas.—If gas is evolved, bring it in contact with lime-water contained in a mushroom trap resting upon the mouth of the test-tube. The precipitation of **$CaCO_3$** indicates CO_3. [Odor of SO_2 indicates presence of SO_3 or S_2O_3 to be tested for later. Separation of S indicates S_2O_3.]

To the clear solution add $BaCl_2$ in excess and filter.



MUSHROOM TRAP.

Precipitate.

$BaSO_4$,$BaSiF_6$. Wash, dry, and divide.

(1) Put a portion in a test-tube, add H_2SO_4, warm, and hold in the fumes a moistened rod. Deposition of white **H_4SiO_4** indicates

SiF_6.

(2) Mix a portion with Na_2CO_3 and heat upon charcoal. Moisten the residue and apply it to a silver coin. A black stain of Ag_2S indicates

SO_4.

Filtrate.

Neutralize with NH_4OH. Precipitation indicates the presence of one or more of the ions,

$$(a)\ \left\{\begin{array}{ll} PO_4 & C_2O_4 \\ AsO_4 & SiO_4\dagger \\ AsO_3 & \end{array}\right\},$$

or, possibly, depending on conditions, one or more of the ions,

$$(b)\ \left\{\begin{array}{ll} BO_3\ddagger & SO_3 \\ CrO_4 & S_2O_3 \\ C_4H_4O_6 & F \end{array}\right\}.$$

No precipitation indicates the absence of the acids of (*a*). Special tests must be made individually for the acids of (*b*) in any event, and for those of (*a*) if a precipitate falls.

[2] Unless arsenic is known to be absent, acidify the solution with HCl, warm, pass H_2S until precipitation is complete, filter, and treat the filtrate according to (1) or (2).

(1) Evaporate to dryness, add HNO_3, evaporate again, extract with dilute HNO_3, filter, add drop by drop to a solution of $(NH_4)_2MO_4$ in HNO_3. P. yellowish **$(NH_4)_3PO_4.11MoO_3.6H_2O$** indicates PO_4.

(2) Evaporate to dryness, desiccate at 110° C., extract with dilute HCl, filter, add NH_4OH in excess and magnesia mixture. P. white, crystalline **NH_4MgPO_4** indicates PO_4.

[3] Acidify the solution, add NH_4OH in excess and magnesia mixture.

---

* In testing for the acidic ions it is understood that sodium and potassium are the only basic ions present.

† SiO_4, the acidic ion of orthosilicic acid H_4SiO_4, is taken as the representative of the many complex ions SiO_3, SiO_4, Si_2O_5, Si_3O_{11}, etc.

‡ BO_3, the acidic ion of H_3BO_3, is here taken as the representative of the ions found in borates—BO_2, BO_3, B_4O_7, etc.

Precipitate.	*Filtrate.*
If PO_4 was not found in [2], P. white, crystalline, NH_4MgAsO_4 indicates AsO_4. If PO_4 was found in [2], filter, wash with dilute NH_4OH, drain on the filter, and add $AgNO_3$. * Reddish brown color, Ag_3AsO_4, shown at once or on addition of a little $HC_2H_3O_2$, indicates AsO_4.	Acidify with HCl, warm, pass H_2S. P. yellow As_2S_3 indicates AsO_3. Should the indication be doubtful, the precipitate may be tested for arsenic by the methods of the basic analysis.

[4] Acidify the solution with HNO_3, boil out CO_2, make the solution faintly ammoniacal, add $CaCl_2$, filter, acidify the filtrate with $HC_2H_3O_2$, and add $Pb(C_2H_3O_2)_2$. If a white precipitate forms ($PbSO_4$), treat it with a strong solution of $NH_4C_2H_3O_2$. P. yellow $PbCrO_4$ indicates

CrO_4.

[5] Evaporate the solution to dryness, ignite strongly and dissolve in water.† Conduct the treatment by (1) or (2), according as chromium is or is not known to be present.

(1) If chromium is known to be absent, acidify slightly with HCl, absorb in turmeric-paper, dry at 100° C., repeating the absorption and drying several times before giving up the attempt to secure a reaction. The formation of a pink coloration indicates probably BO_3. Touch the stain with a drop of a solution of Na_2CO_3 or NH_4OH. Change of color to black or dark green confirms BO_3.

(2) In case CrO_4 is known to be present, acidify with HCl, add H_2SO_3, boil out the excess of SO_2, neutralize with Na_2CO_3, filter, acidulate the filtrate slightly with HCl, and make the test with turmeric-paper as directed in (1). Pink coloration changed to black or dark green by Na_2CO_3 or NH_4OH indicates

BO_3.

[6] Acidify the solution with HCl, add $BaCl_2$, filter, pass H_2S, filter, boil out H_2S, add Na_2CO_3 in considerable excess, boil out all free NH_3, taking care to have enough Na_2CO_3 present to break up ammonium salts, filter, neutralize the filtrate carefully with HCl, boil out CO_2, make just alkaline with NH_4OH, add $HC_2H_3O_2$ in distinct but not large excess, and then $CaCl_2$, filter and wash.

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* If chromic acid is present, it may be necessary to dissolve the precipitate by magnesia mixture in HCl and reprecipitate by NH_4OH to remove all traces of chromate, which would also give a reddish color with $AgNO_3$.

† If it is known that a chlorate is not present, the evaporation and ignition may be omitted.

Precipitate.

CaF_2, CaC_2O_4. Divide.

(1) Dissolve in HCl, reprecipitate by NH_4OH, filter, wash, treat the precipitate with dilute H_2SO_4, heat to boiling, add drop by drop a solution of $KMnO_4$. Bleaching indicates

C_2O_4.

(2) Dry, mix with an equal amount of an alkali silicate, add strong H_2SO_4, warm, test the fumes with a moistened rod. Deposition of white **H_4SiO_4** indicates

F.

Filtrate.

Add more $CaCl_2$, make faintly alkaline with NH_4OH, cool, shake, set aside for ten minutes. If a precipitate forms, filter, wash, transfer the precipitate to a test-tube, digest in cold KOH, filter. Boil the filtrate. P. white, formed on boiling, dissolved again on cooling, indicates

$C_4H_4O_6$.

Put the precipitate into a carefully cleaned test-tube, add a single drop of NH_4OH and then a little $AgNO_3$, and warm. The formation of a silver mirror confirms

$C_4H_4O_6$.

[7] To the solution add $Zn(C_2H_3O_2)_2$ until precipitation ceases, filter, and wash.

Precipitate.

Treat with dilute HCl, warm gently, and test the fumes with paper moistened with $Pb(C_2H_3O_2)_2$. The formation of brown or black **PbS** indicates

S.

Filtrate.

Dilute, acidulate with $HC_2H_3O_2$, add $BaCl_2$ in excess and filter.

Precipitate.

$BaSO_4$ indicates SO_4.

Filtrate.

Add iodine until color is permanent, add HCl and bleach with a few drops of $SnCl_2$.

Precipitate.

$BaSO_4$ indicates SO_3.

Filtrate.

Add bromine water until color is permanent, bleach with $SnCl_2$.

Precipitate.

$BaSO_4$ indicates

S_2O_3.

[8] Add dilute HCl to the solution, evaporate to dryness. The formation of the characteristic hydrogel during the evaporation is indicative of SiO_4 and derivatives.

(1) Fuse the residue in a bead of $NaPO_3$. Insolubility in fused bead indicates

SiO_4.

(2) Dry, mix with an equal amount of a fluoride and treat as in [6], (2). Deposition of white **H_4SiO_4** indicates

SiO_4.

COMMENTARY UPON GROUP I.

The acidic ions of this group may be subdivided into three classes: (1) those whose barium salts are not acted upon by hydrochloric acid—SO_4 and SiF_6; (2) those whose barium salts are acted upon by hydrochloric acid, but are reprecipitated on neutralization of the hydrochloric acid by ammonium hydroxide—PO_4, AsO_4, AsO_3, C_2O_4, CO_3, SiO_4 *; (3) those whose barium salts are acted upon by hydrochloric acid and are not completely reprecipitated by ammonium hydroxide,—BO_3, CrO_4, $C_4H_4O_6$, SO_3, S_2O_3, F.

[1] In testing for SiF_6 the barium precipitate should be thoroughly dried and placed in a dry test-tube, as the presence of moisture either in the precipitate or on the tube will make the test upon the glass rod less delicate.

[2] Before testing for PO_4 hydrogen sulphide is passed into the solution for a sufficient length of time to insure the removal of AsO_4, which with molybdic acid and magnesium mixture reacts similarly to PO_4. After the treatment with hydrogen sulphide the evaporation with nitric acid is to remove hydrochloric acid and silica, and to oxidize organic matter and reducing agents which would interfere with the formation of the insoluble phospho-molybdate. In the second test for PO_4 the desiccation at 110° C. is to remove any silica which may be present.

[3] In this test the precipitate obtained with magnesium-chloride mixture should be carefully washed, because the presence of any CrO_4 here would interfere with the test for AsO_4 by yielding reddish brown $AgAsO_4$.

[4] Nitric acid is chosen for the removal of carbonates

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* Typical.

rather than hydrochloric acid, because of the possible reducing action of hydrochloric acid upon CrO_4. The carbon dioxide is boiled out to prevent the precipitation of lead carbonate on neutralization with ammonium hydroxide, and calcium chloride is added to remove C_2O_4 and $C_4H_4O_6$, which, like CrO_4, give insoluble precipitates with lead acetate.

[5] Chlorates and chromates if present must be removed to avoid their oxidizing action upon the turmeric dye when acid is added. The chlorates are decomposed by heat, leaving chlorides. By the action of sulphurous acid chromic acid is reduced, and sodium carbonate precipitates the chromic hydroxide.

[6] The addition of barium chloride in acid solution removes SO_4 and SiF_6, if present; hydrogen sulphide removes AsO_3 and AsO_4; and the excess of hydrogen sulphide is boiled out to avoid its oxidation to the sulphate, and also to avoid the possibility of the formation of silver sulphide when silver nitrate is added. Sodium carbonate is used to remove the excess of the barium salt, and ammonium salts are removed because of their tendency, when present in considerable amount, to prevent the complete precipitation of fluorides and tartrates. The sodium carbonate should be added in considerable excess, not only to aid in the removal of the ammonium salts, but also to prevent the precipitation of barium salts of F, C_2O_4, and $C_4H_4O_6$. The filtrate is acidulated with hydrochloric acid to decompose the excess of sodium carbonate, and the carbon dioxide is boiled out to prevent subsequent precipitation of calcium carbonate. Care is taken to avoid using a large excess of hydrochloric acid, because of the necessity of using a corresponding amount of ammonium hydroxide in making alkaline, a procedure which would result in the introduction of a considerable amount of ammonium salt. Acetic acid is used in moderate excess, because the calcium salts of F and C_2O_4 are not

wholly unacted upon by the acid if present in any considerable amount. It is well to avoid the addition of a large excess of calcium chloride, because of the tendency of the calcium tartrate to form also under such conditions. The treatment of the calcium precipitate with hydrochloric acid and the reprecipitation by ammonium hydroxide is to eliminate any calcium tartrate which may have been precipitated.

In the mirror test for $C_4H_4O_6$ the test-tube used must be very carefully cleaned.

[7] Some indication of SO_3 and S_2O_3 has already been given when the solution was acidified in test [1]. At this point the chief object is to furnish means for the detection of SO_3 when present with S_2O_3.

Zinc acetate is added to remove any S which may be present with the compounds of the ions of this group. The acidulation with acetic acid is to obtain the proper conditions for the precipitation of barium sulphate and for the prevention of the formation of barium sulphite and barium thiosulphate. Acetic acid is used rather than hydrochloric acid, because it is less apt to decompose the S_2O_3 into SO_3 and S. Barium chloride is added in excess in order to have enough of that reagent present to react with SO_4 formed by the addition of iodine and bromine. The iodine and bromine colors are bleached with stannous chloride, because the precipitated barium sulphate is more easily detected in the absence of these colors.

[8] Careful desiccation is important in order to obtain the insoluble silica. The insoluble skeleton of silica is best observed while the bead is in a state of fusion.

Certain acidic ions of Group I are mutually exclusive in an acidulated solution. Thus, the ions CrO_4 and AsO_4 are oxidizers, while the ions AsO_3, C_2O_4, $C_4H_4O_6$, SO_3, and S_2O_3 are reducers. The analysis of mixtures containing such ions requires special treatment.

CHARACTERISTIC REACTIONS OF ACIDIC IONS.

GROUP II.

REAGENT.	$BaCl_2$	$CaCl_2$	$AgNO_3$	$Pb(C_2H_3O_2)_2$	Special tests.
TYPICAL COMPOUND. *Na*Cl	....	....	P. white **AgCl**. Sol. in NH_4OH. Insol. in HNO_3.	P. white $\mathbf{PbCl_2}$. Sol. in *hot* H_2O.	Mixture of H_2SO_4 + MnO_2 evolves chlorine. Mixture of H_2SO_4 + $K_2Cr_2O_7$ evolves CrO_2Cl_2.
*K*Br	....	....	P. yellowish white **AgBr**. Somewhat sol. in NH_4OH.	P. white $\mathbf{PbBr_2}$. Sol. in *hot* H_2O.	Chlorine liberates Br, which is best collected in $CHCl_3$.
*K*I	....	....	P. yellow **AgI**. Nearly insol. in dilute NH_4OH.	P. yellow $\mathbf{PbI_2}$. Sol. in *hot* H_2O.	Cl or N_2O_3 liberates I, best collected in $CHCl_3$ or tested for by starch.
*K*CN	....	....	P. white **AgCN**. Sol. in excess. " NH_4OH. Insol. in HNO_3.	P. white. Sol. in HNO_3.	Mixture of $FeSO_4$ + $FeCl_3$ added to an alkali cyanide and acidified with HCl gives Prussian blue $(Fe_2)_2Fe_4C_{18}N_{18}$.

*K_4*Fe(CN)$_6$	....	....	P. white. Sol. in KCN. Insol. in HNO_3. Insol. in NH_4OH of moderate strength and on short exposure.	P. white.	With ferric salts gives Prussian blue. With salts of copper gives brown-red precipitate.
*K_3*Fe(CN)$_6$	....	....	P. reddish brown. Sol. in NH_4OH. Sol. in KCN. Insol. in HNO_3.	No P., unless in alkaline solution, when sometimes **PbO_2** (dark brown) is thrown down.	With ferrous salts gives Turnbull's blue.
*K*SCN	....	....	P. white. Difficultly sol. in NH_4OH.	P. white.	With ferric salts gives blood-red color. Bleached by $HgCl_2$.
*Na_2*S	....	....	P. black. Sol. in hot HNO_3.	P. black. Sol. in hot HNO_3.	Sulphides heated with Na_2CO_3 on charcoal yield Na_2S, which, moistened, blackens silver coin.

IDENTIFICATION OF THE ACIDIC IONS OF GROUP II.

[1] Acidify the solution with dilute HNO_3. The odor of H_2S indicates S in a sulphide, and the odor of HCN (*smell cautiously!*) indicates CN. Add $AgNO_3$. The formation of a precipitate indicates acidic ions of this group.

White $Ag_4FeC_6N_6$	indicates	$\overset{II}{Fe}C_6N_6$.
Orange $Ag_3FeC_6N_6$	"	$\overset{III}{Fe}C_6N_6$.
White $AgSCN$	"	SCN.
White $AgCN$	"	CN.
Black Ag_2S	"	S.
Yellow AgI	"	I.
Pale yellow $AgBr$	"	Br.
White $AgCl$	"	Cl.
White $AgNO_2$	"	NO_2.

The absence of a precipitate indicates the absence of every member of the group excepting NO_2, $AgNO_2$ being soluble in hot water and sparingly soluble in cold water.

[2] Test individual portions of the solution as follows:

(1) Acidify with HCl and add $FeCl_3$. (*a*) Blue $\overset{III}{Fe}_4\overset{II}{Fe}_3C_{18}N_{18}$ indicates

$\overset{II}{Fe}C_6N_6$.

(*b*) Red color, in absence of an iodide or nitrite, is $FeS_3C_3N_3$, and indicates

SCN.

(*c*) If the indication is doubtful, owing to a mixture of the blue and red colors, add $HgCl_2$ which will bleach the red $FeS_3C_3N_3$ and bring out the blue $\overset{III}{Fe}_4\overset{II}{Fe}_3C_{18}N_{18}$, if $\overset{II}{Fe}C_6N_6$ is present.

(2) Acidify with HCl and add $FeSO_4$. Blue $\overset{II}{Fe}_3\overset{III}{Fe}_2C_{12}N_{12}$ indicates

$\overset{III}{Fe}C_6N_6$.

(3) In case the indication of (1) was doubtful as to SCN, acidify with dilute H_2SO_4, add $SnCl_2$ (enough), and boil in a test-tube fitted with a mushroom trap containing $FeCl_3$. The formation of the red $FeS_3C_3N_3$ indicates

SCN.

(4) In case neither $\overset{II}{Fe}C_6N_6$, nor $\overset{III}{Fe}C_6N_6$, nor SCN has been indicated, add a mixture of $FeCl_3+FeSO_4$, and acidulate with HCl. Blue * $\overset{III}{Fe_4}\overset{II}{Fe_3}C_{18}N_{18}$ indicates

CN.

In case either $\overset{II}{Fe}C_6N_6$, or $\overset{III}{Fe}C_6N_6$, or SCN has been indicated, neutralize exactly with HCl, add solid $HNaCO_3$, and distil. Add $FeCl_3+FeSO_4$ to the distillate, treat with NaOH in excess, and then acidify with HCl. Blue $\overset{III}{Fe_4}\overset{II}{Fe_3}C_{18}N_{18}$ indicates

CN.

[3] Acidify faintly with acetic acid, add $Zn(C_2H_3O_2)_2$ until precipitation ceases, filter and wash. Treat a portion of the precipitate with dilute HCl, warm gently, and test the fumes with paper moistened with $Pb(C_2H_3O_2)_2$. The formation of brown or black **PbS** indicates

S.

[This test is best made in connection with the tests of Group I, [7]].

[4] If no cyanide or sulphide has been indicated, the solution is ready for treatment. If a cyanide (simple or complex) or a sulphide has been indicated, evaporate a portion of the solution to dryness, fuse the residue with Na_2CO_3 and enough KNO_3 to insure oxidation. Dissolve the fused mass in water. Divide the solution.

(1) Acidify with HNO_3 and add $AgNO_3$.

A precipitate of yellow **AgI** indicates I.
" " " pale yellow **AgBr** indicates Br.
" " " white **AgCl** indicates Cl.

If no precipitation takes place the absence is proved of

I, Br, and Cl.

(2) In case any precipitation takes place in (1) acidify with H_2SO_4, add a drop or two of KNO_2, and shake with $CHCl_3$. The development of the violet color of iodine indicates

I.

(3) If I was not indicated in (2), acidify with dilute H_2SO_4, introduce $CHCl_3$, and add chlorine water carefully drop by drop while shaking. The development of the yellow or reddish yellow color of bromine indicates

Br.

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* In case the iron salts are used in excess the color may be green (mixture of yellow and blue). The blue color becomes apparent upon filtering, $\overset{III}{Fe_4}\overset{II}{Fe_3}C_{18}N_{18}$ remaining upon the filter.

(4) If I was indicated in (2), acidify with H_2SO_4, add KNO_2 in solution, drop by drop, to the boiling mixture, until all iodine is set free and expelled. The failure of the escaping steam to develop a characteristic gray color upon red litmus paper is proof of the removal of the free iodine. Cool, introduce $CHCl_3$ and add chlorine water drop by drop while shaking. The development of the yellow or reddish yellow color of bromine indicates

Br.

(5) If neither I nor Br has been indicated the precipitate obtained in (1) must have been AgCl, indicative of

Cl.

If I has been indicated in (2), treat with H_2SO_4, add KNO_2 gradually, and boil until all iodine is set free and expelled. The solution thus freed from iodine, or the original solution containing no iodide, is to be made alkaline with Na_2CO_3 and evaporated to dryness in a test-tube. To the residue add dry $K_2Cr_2O_7$ or K_2CrO_4 and a little strong H_2SO_4. Heat gently and collect the fumes in a moistened trap. Wash out the trap with a very little water, add NH_4OH in slight excess, warm gently, acidify with $HC_2H_3O_2$, and add $Pb(C_2H_3O_2)_2$. If a white precipitate forms, add a little strong $NH_4C_2H_3O_2$. The formation of yellow $PbCrO_4$ indicates

Cl.

COMMENTARY UPON GROUP II.

Two of the acidic ions of this group, S and NO_2, are best tested for under Groups I and III respectively. From the other members of the group, S is easily distinguished by the fact that it forms the only black silver salt in the group. The ion NO_2 does not generally appear in this group, because its silver salt is fairly soluble in water, and is precipitated only in concentrated solutions. The other members of the group readily divide themselves into two classes: (1) the cyanogen ions, and (2) the halogen ions.

Test [1] informs us in a general way of the presence or absence of members of this group. A white precipitate indicates $Fe^{III}(CN)_6$, I, or Br, with or without the acidic ions which give white silver salts. A black precipitate indicates S, with or without the other members of the group. No precipitate indicates the absence of the group with the possible exception of NO_2.

In test [2] (1) and (2), the best results are obtained by using very dilute solutions. In (3) advantage is taken of the volatility of sulphocyanic acid in separating SCN from $Fe^{II}(CN)_6$ and $Fe^{III}(CN)_6$. The stannous chloride is used to take up iodine and bromine possibly set free if bromides and iodides are present. In (4) the hydrocyanic acid is liberated by the carbonic acid formed from the acid sodium carbonate, and passes to the distillate.

Test [3] has been discussed under Group I, [7].

In test [4] the cyanides and sulphides are removed, because their ions and the halogen ions form insoluble silver salts under like conditions. In the fusion process the cyanides are converted to carbon dioxide and nitrogen, and the sulphides to sulphates. The iron is separated as the oxide and filtered off. In (4) the nitrous acid formed in the interaction of potassium nitrite and sulphuric acid liberates iodine which is removed by boiling. Care must be taken to add the nitrite gradually, and not to continue the addition after all of the iodine has been liberated. Though bromine may also be volatilized to some extent with the iodine, it is nevertheless true that the amount thus removed is proportionate to the amount originally present, and that enough is left to permit a correct inference as to the quantity originally present. In (5), after the removal of the iodine the solution is made alkaline with sodium carbonate to convert the volatile hydrochloric acid to sodium chloride, which will not volatilize on heating. The evaporation must be carried to dryness, because the formation of chlorochromic anhydride on addition of sulphuric acid to potassium dichromate and sodium chloride can take place only in the absence of water. Special care should be observed to avoid spattering chromic acid into the trap, as this would vitiate the test. When the chlorochromic anhydride is acted upon by water in the trap, it is hydrolyzed to hydrochloric acid and chromic acid. The ammonium hydroxide is added to neutralize free hydrochloric acid and sulphuric acid, the presence of which might interfere with the precipitation of lead chromate; and acetic acid, which does not interfere with the precipitation, is used to neutralize the ammonia. The white precipitate of lead sulphate, which may form, is due to the presence of sulphuric acid in the trap.

CHARACTERISTIC REACTIONS OF ACIDIC IONS.

GROUP III.

REAGENT. TYPICAL COMPOUND.	$BaCl_2$	$CaCl_2$	$AgNO_3$	$Pb(C_2H_3O_2)_2$	Special tests.
KNO_3	....	....	....	....	A nitrate dissolved in dilute H_2SO_4 and mixed with $FeSO_4$ gives black color when acted on by strong H_2SO_4. With $MnCl_2$ in strong HCl gives black color on warming.
$KClO_3$	....	....	....	....	Deflagrates on charcoal. Evolves greenish fumes (more or less explosive) with strong H_2SO_4.
KNO_2	....	....	P. white in strong solutions. Sol. in *hot* water.	....	With HCl sets free I from iodides, bleaches $KMnO_4$, forms from $C_6H_4(NH_2.HCl)_2$ yellow $C_{12}H_{13}N_5$ (phenylene brown).
$KOCl$	....	....	....	....	In presence of acids, without heating, liberates I from iodides. Evolves Cl with $HC_2H_3O_2$. Darkens $MnCl_2$ in strong HCl on warming. Oxidizes metallic Hg to yellow HgO.
$NaC_2H_3O_2$	....	....	P. white. Sol. in *hot* water.	....	On addition of a ferric salt, neutralization and boiling, acetates precipitate basic ferric acetate, reddish brown. Heated with H_2SO_4 and C_2H_5OH or $C_5H_{11}OH$, characteristic odor is developed.

IDENTIFICATION OF THE ACIDIC IONS OF GROUP III.

[1] Add to a portion of the solution twice its volume of a saturated solution of $MnCl_2$ in the strongest HCl, and warm gently. The formation of a dark coloration ($MnCl_4$ or Mn_2Cl_6) is due to the presence of some oxidizing agent. The absence of the dark coloration proves the *absence* of oxidizing agents, and so of the acidic ions

$$NO_2, NO_3, ClO, ClO_3.$$

If a dark coloration appears proceed with tests [2], [3], [4], [5]. Test [6] must be made in any case.

[2] Dilute a portion of the solution abundantly, add a few drops of $C_6H_4[NH_2.HCl]_2$ and acidify. The production of a yellow color at once or after some time indicates

$$NO_2.$$

[3] Acidify a portion of the solution with H_2SO_4, add KI in amount sufficient to break up a nitrite, if present, and boil out the NO evolved. Add NaOH, boil out all NH_3, treat with Fe+Zn (1:3), and again boil. The evolution of NH_3 indicates

$$NO_3.$$

If it has been shown in [2] that no nitrite is present the treatment with H_2SO_4 and KI may be omitted.

[4] To a portion of the solution add a small globule of mercury and shake. Formation of yellowish brown HgO on the surface of the mercury indicates

$$ClO.$$

[5] If ClO was indicated add to another portion of the filtrate HNO_3 in slight excess, enough KI to decompose all hypochlorite present, KNO_2 sufficient to destroy the excess of KI, and boil out the iodine evolved. Add $AgNO_3$, filter, treat with Na_2CO_3 in slight excess, filter, evaporate to dryness, ignite, extract the residue with hot water, acidulate with HNO_3, and add $AgNO_3$. Precipitation of white **AgCl** indicates

$$ClO_3.$$

If ClO was shown to be absent, the treatment with KI and KNO_2 is omitted and the test begun with the addition of $AgNO_3$.

[6] (1) Acidify a small portion (5 cm.³) of the solution with dilute H_2SO_4 and heat to boiling. Cool, add a few cms.³ of ethyl alcohol or amyl alcohol, and introduce cautiously a volume of strong H_2SO_4 equal to that of the rest of the liquid. Heat gently, then cool. The development of a characteristic ethereal odor of ethyl acetate or amyl acetate indicates

$$C_2H\ O_2.$$

(2) Acidify a portion of the solution with HCl, add $FeCl_3$, and treat with NH_4OH to exact neutrality. The formation of a deep-red solution suggests the presence of ferric acetate. Add HCl to very slight acidity, dilute abundantly, and boil. The precipitation of reddish brown basic ferric acetate indicates

$$C_2H_3O_2.$$

If both (1) and (2) give doubtful indications, on account of interfering complications, distil a portion of the solution and apply these tests to the distillate.

COMMENTARY UPON GROUP III.

The compounds of the acidic ions of Group III, with the exception of $C_2H_3O_2$, are oxidizing agents.

[1] The test with manganese chloride and hydrochloric acid indicates simply the presence or absence of oxidizing agents. If the dark coloration is obtained, the ions of this group which are oxidizing agents are to be tested for, as well as $C_2H_3O_2$. If no dark coloration is obtained, the only member of the group possibly present is $C_2H_3O_2$.

[2] The abundant dilution of the solution before the addition of the phenylene diamine hydrochloride is advisable, on account of the extreme delicacy of the test.

[3] The hydrogen formed in alkaline solution by the action of sodium hydroxide upon the iron and zinc couple reduces the NO_3, if present, to ammonia; the formation of ammonia therefore indicates the presence of NO_3. In order, however, that the test may be trustworthy, ammonium salts must be broken up and the ammonia removed before the reduction with hydrogen is begun. This is done by boiling with sodium hydroxide. Special care must be taken to avoid any spattering of the alkaline liquid upon the litmus-paper.

[4] Mercuric oxide is best precipitated by the action of mercury upon salts of ClO, when the solution is neutral or alkaline and well shaken.

[5] If ClO is present it must be removed, on account of its tendency to form Cl and ClO_3. The nitric acid should be added in *faint* excess, on account of the possibility of the

oxidation of ClO to ClO_3, and because of its decomposing action upon potassium iodide. The potassium iodide must be added gradually, in order to avoid an unnecessary excess, which in turn would involve the use of a large amount of potassium nitrite to effect its removal. The silver nitrate is added to remove the I or Cl which may be present, and the sodium carbonate to remove the silver nitrate. The ignition reduces ClO_3 to Cl. The solution is finally acidified with nitric acid to decompose any excess of sodium carbonate present.

[6] (1) The preliminary treatment with sulphuric acid breaks up hypochlorites and nitrites, which would tend to mask the ethereal odors by evolution of chlorine and oxides of nitrogen. The development of the ethereal odors may require a little time; they become more distinct upon shaking the cooled solution. (2) As neutral solutions of ferric salts in general tend to separate basic salts on heating, the directions should be followed closely. Faint acidity and abundant dilution are the best conditions under which to form the insoluble basic acetate.

THE COMPLETE ACIDIC ANALYSIS.

The following procedure is to be used when solutions containing members of the different acidic groups are to be examined:

[1] Acidify a portion of the solution with HCl.

Evolution of Gas.

CO_2 indicates CO_3.
SO_2 " SO_3.
SO_2+S " S_2O_3.
N_2O_3 " NO_2.
Cl " ClO.
HCN " CN.

[2] Acidify a portion of the solution with HCl, filter if necessary, and to the clear solution add $BaCl_2$ in excess.

Precipitate.—Distinguish between SO_4 and SiF_6 as in Group I.

Filtrate.—Neutralizo with NH_4OH.

If a precipitate forms, distinguish between PO_4, AsO_4, AsO_3, C_2O_4, SiO_4, as in Group I.

In any event test for BO_3, CrO_4, $C_4H_4O_6$, SO_3, S_2O_3, as in Group I.

[3] Acidify another portion with HNO_3 and add $AgNO_3$. If a precipitate forms, proceed as in Group II, [1].

[4] To another portion add $MnCl_2+2HCl$ as directed in Group III [1]. If a coloration is produced, all the acidic ions of Group III are to be tested for. If no coloration appears, only $C_2H_3O_2$ is to be tested for.

PART IV.

THE SYSTEMATIC EXAMINATION.

The detection separately of basic ions and acidic ions of soluble compounds has been discussed. The problem involving the identification of elementary substances and their compounds, soluble and insoluble, with the detection of basic ions and acidic ions in the same compound, is now to be considered. This part of the work is naturally divided into

(1) *The Preliminary Testing,*
(2) *The Preparation for Analysis,*
(3) *The Analysis.* (Already treated in Parts II and III.)

In the practical examination of an unknown substance, the Preliminary Testing and the Preparation for Analysis naturally precede.

The substances which fall within the range of our systematic scheme of analysis are the commoner chemical elements and compounds, excluding for the most part the compounds of carbon, the analysis of which demands intimate knowledge of Organic Chemistry. The commoner compounds of carbon which are considered in this scheme are the carbon oxides and carbonates; oxalic acid and oxalates; acetic acid and acetates; tartaric acid and tartrates; hydrocyanic acid and the cyanides, simple and complex. For the systematic detection of the numerous compounds of carbon and the rarer elements reference must be made to special treatises. In Part V, however, are given directions for the elementary analysis of pure organic compounds, and characteristic reactions and special tests for the proximate determination of a few characteristic carbon compounds.

PRELIMINARY TESTING.

A. SOLIDS.

	TREATMENT.	OBSERVATION.		INDICATION.
I	Observe carefully the physical properties—structure, color, luster, etc.			Draw inferences provisionally according to previons experience.
II	Heat in a closed tube.	*a.* Change of color:		Presence or formation of
		Yellow, hot; nearly white, cold.		ZnO
		Yellow to red, hot; yellow, cold; fusible.		PbO
		Yellowish brown, hot; dirty white, cold.		SnO_2
		Orange-yellow, hot; pale yellow, cold; fusible.		Bi_2O_3
		Dark red to black, hot; brown-red, cold.		Fe_2O_3
		Yellow to dark red; fusible.		$PbCrO_4$
		Blackening accompanied by evolution of inflammable gas, water, and empyreumatic odor.		Organic matter.
		b. Evolution of volatile matter:		
		Kindling glowing wood—	O_2	Chlorate, nitrate, peroxide, or unstable oxide.
		Odor of burning sulphur—	SO_2	Sulphur, sulphide, sulphate (with reducing matter), or other compound of sulphur.
		Yellowish or brownish red color, characteristic odor—	N_2O_3,N_2O_4	Nitrate, nitrite.

PRELIMINARY TESTING (*Continued*).

	TREATMENT.	OBSERVATION.		INDICATION.
II	Heat in a closed tube.	*b.* Evolution of volatile matter:		
		In some oxidizing mixtures:		
		Greenish color, characteristic odor—	Cl_2	Chloride.
		Reddish color, characteristic odor—	Br_2	Bromide.
		Violet color, characteristic odor, black sublimate—	I_2	Iodide.
		Characteristic odor—	H_2S	Sulphide or other compound of sulphur, with water or organic matter.
		Peach-blossom flame, characteristic odor—	C_2N_2	Cyanide.
		Colorless, making lime-water or baryta-water turbid—	CO_2	Carbonate, organic matter.
		Inflammable with empyreumatic odor—		Organic matter.
		Characteristic odor, turning red litmus blue—	NH_3	Ammonium compound.
		Condensing to transparent liquid—	H_2O	Water held mechanically, in crystalline salt, or chemically (organic matter).
		—if acid in reaction		Volatile acid or acid salt.
		—if alkaline in reaction		Ammonium compound.
		c. Formation of a sublimate:		
		Black—	As_4	Arsenic.
		Black, violet vapor—	I_2	Iodine.
		Black, red when rubbed—	HgS	Mercuric sulphide.
		White, yellow when hot—	Hg_2Cl_2	Mercurous chloride.
		White, crystalline,	$HgCl_2$	Mercuric chloride.
		White, crystalline,	As_2O_3	Arsenious oxide.
		White, crystalline,	Sb_2O_3	Antimonious oxide.
		White—		Ammonium salts, some organic substances.

		Yellow—	As_2S_3	Arsenious sulphide.
		Yellow, red when rubbed—	HgI_2	Mercuric iodide.
		Yellow, melting to dark liquid—	S_6	Sulphur.
		Metallic mirror or globules—	Hg	Mercury.
III	Addition of water in a test-tube.	*a.* Evolution of gas:		
		Colorless, odorless, inflammable—	H_2	Alkali or alkali earth metals.
		Colorless, odorless, supports combustion—	O_2	Peroxides.
		Colorless, characteristic odor, luminous flame—	C_2H_2, etc.	Metallic carbides.
		Colorless, characteristic odor, turns red litmus blue—	NH_3	Nitrides of alkali earths.
		Colorless, garlic odor, inflammable—	PH_3	Phosphides of alkalies and alkali earths.
		Colorless, characteristic odor—	H_2S	Sulphides of Al, Mg, etc.
		Colorless, odorless, turns blue litmus red—	HCl, HBr, HI	Halides of negative elements, *e.g.*, PBr_3, PCl_5, etc.
		b. Change of color (non-crystalline to crystalline by hydration).		Certain anhydrous salts, *e.g.*, $CuSO_4$, $CuCl_2$, etc.
		c. Change of form (crystalline to non-crystalline by hydrolysis).		Certain salts which readily become basic, *e.g.*, Bi and Sb salts.
IV	Warm gently with concentrated H_2SO_4 in a test-tube.	Evolution of gas:		
		Odor of burning sulphur—	SO_2	Sulphite or thiosulphate.
		Yellowish or brownish red color, characteristic odor—	N_2O_3, N_2O_4	Nitrate, nitrite.
		Greenish color, characteristic odor—	Cl_2	Hypochlorite, chlorate.
		Greenish color, characteristic odor, explosive—	ClO_2	Chlorate.*
		Reddish color, characteristic odor—	Br_2	Bromide.
		Violet color, characteristic odor, black deposit—	I_2	Iodide.
		Characteristic odor—	H_2S	Sulphide.

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* Use a very small crystal.

PRELIMINARY TESTING (*Continued*).

	TREATMENT.	OBSERVATION.	INDICATION.
IV	Warm gently with concentrated H_2SO_4 in a test-tube.	Evolution of gas;	
		Colorless, making lime-water or baryta-water turbid— CO_2	Carbonate, oxalate.
		Colorless, burning with blue flame— CO	Cyanide (simple or complex), oxalate.
		Colorless, fuming and depositing silica on contact with water— SiF_4	Fluosilicate, or fluoride with silica or silicate.
		Characteristic odor, turning blue litmus red— HCl	Chloride.
		Characteristic odor, turning blue litmus red, etching glass— HF	Fluoride.
		Characteristic odor, turning blue litmus red— $HC_2H_3O_2$	Acetate.
		Charring—	Organic matter.
V	Heat on charcoal.	*a.* The substance melts and runs into the charcoal.	Salts of Na, K, Li, [Rb, Cs].
		b. The residue is infusible:	
		on moistening with water is alkaline to litmus—	BaO, SrO, CaO, MgO.
		on moistening with solution of Co $(NO_3)_2$ and reheating gives —blue	Al_2O_3.
		—pale blue	SiO_2.
		—green	ZnO.
		(difficult)—pink	MgO.
		c. The substance deflagrates.	Chlorates, nitrates.
		d. A coating is formed on the charcoal:	
		White, odor of garlic— As_2O_3	Arsenic.
		White (near the residue)— Sb_2O_3	Antimony.
		Yellow, hot; white, cold— ZnO	Zinc.
		Yellow to red, hot; yellow, cold— PbO	Lead.
		Yellowish brown, hot; dirty white, cold; very near the residue— SnO_2	Tin.

		Orange-yellow, hot; pale yellow, cold—	Bi_2O_3	Bismuth.
		Reddish brown to orange—	CdO	Cadmium.
		Dark red—(difficult)	Ag	Silver.
VI	Heat on charcoal with Na_2CO_3 and powdered charcoal.	A residue remains:		
		Metallic globule without coating—		Gold, copper.
		Metallic globule with coating as in IV—		Silver, lead, tin, bismuth.
		Magnetic—		Iron, cobalt, nickel.
VII	Heat in borax bead.	The bead is colored:		
		Reducing flame.	*Oxidizing flame.*	
		Blue	Blue	Cobalt.
		Red (opaque)	Blue	Copper.
		Green	Green	Chromium.
		Bottle-green	Yellow	Iron.
		Gray (opaque)	Reddish brown	Nickel.
		Colorless or gray	Colorless or yellow	Bismuth.
		Colorless	Amethyst-red	Manganese.
VIII	Heat on graphite (a pencil point).	The flame is colored:		
		Yellow		Sodium.
		Violet		Potassium.
		Carmine		Lithium.
		Crimson		Strontium.
		Orange-red		Calcium.
		Green, bright		Copper.
		Green, distinct		Boric acid.
		Green, yellowish		Barium.
		Blue, bright		Cupric chloride.
		Blue, pale		Arsenic.
IX	Heat in bead of $NaPO_3$.	The substance decomposes, but leaves a floating skeleton of silica in colorless or colored glass.		Silica, or a silicate.

PRELIMINARY TESTING (*Concluded*).

B. LIQUIDS.

	TREATMENT.	OBSERVATION.	INDICATION.
I	Test reaction to litmus.	The solution is acid.	Free acid, acid salt, or neutral salt acid to litmus.
		The solution is alkaline.	Free alkali, free alkali earth, salt of an alkali base with a weak acid (carbonate, cyanide, sulphide).
II	Evaporate to dryness on a watch-glass or on platinum foil.	Inflammability of vapor, empyreumatic odor, charring of the residue.	Organic matter.
	Examine residue left on evaporation by methods of A.	Phenomena as in A.	As in A.

C. GASES.

I	Observe color and odor.	Green color, characteristic odor.	Chlorine.
		Reddish yellow color, characteristic odor.	Bromine.
		Reddish yellow color, characteristic odor.	Nitrogen trioxide, nitrogen tetroxide.
		Violet color, characteristic odor.	Iodine.
		Colorless, characteristic odor.	Cyanogen.
		Colorless, becoming yellowish or reddish on contact with air.	Nitrogen dioxide.

		Colorless, characteristic odor.	Ammonia.
		Colorless, characteristic odor.	Hydrogen sulphide.
		Colorless, characteristic odor.	Sulphur dioxide.
II	Test inflammability and action on glowing wood.	*a.* The gas is inflammable:	
		Flame colorless.	Hydrogen.
		Flame yellow.	Organic compound.
		Flame blue.	Carbon monoxide, hydrogen sulphide.
		Flame the color of peach blossoms.	Cyanogen.
		b. The gas does not burn, but kindles glowing wood.	Oxygen; nitrogen monoxide, trioxide, tetroxide.
III	Test action on lime-water or baryta-water.	Turbidity is produced.	Carbon dioxide.
IV	Test action on litmus.	Color destroyed.	Chlorine. Bromine.
		Color red, or destroyed.	Sulphur dioxide.
		Color blue.	Ammonia.
V	Test action on a strong solution of ferrous sulphate.	The solution darkens.	Nitrogen oxides.
VI	Test action upon paper moistened with lead acetate.	The paper is browned, or blackened.	Hydrogen sulphide.
VII	Test action upon paper moistened with starch paste.	The paper is colored blue.	Iodine.

COMMENTARY UPON THE PRELIMINARY TESTING.

While the Preliminary Testing should not be expected to give very certain or definite results, it is often helpful in directing the process of identification.

I. *Examination of physical properties.*—The observation of the structure of the substance, its crystalline or non-crystalline character, its crystal form, its color and luster, is often useful. Metallic luster on a polished surface or crystal face is a general characteristic of metals and alloys. To be seen to the best advantage the substance should be spread out upon a white surface.

II. *Heating in closed tube.*—Three kinds of phenomena are to be looked for in this treatment: (*a*) change of color, (*b*) evolution of volatile matter, and (*c*) formation of a sublimate. It is important to test for volatile matter before continued heating expels it entirely.

III. *Addition of water in a test-tube.*—The best results are obtained by gradual addition of the water and prompt testing of any gas that may be evolved.

IV. *Heating with sulphuric acid.*—Care should be observed not to heat the acid to its fuming-point, because the fumes would interfere seriously with the detection of many volatile products.

V. *Heating on charcoal.*—In (*b*), when treating with cobaltous nitrate, use a very dilute solution. If an excess of the reagent is used, the black cobaltic oxide formed obscures the colors.

VI. *Heating with sodium carbonate on charcoal.*—Have the substances thoroughly mixed with sodium carbonate and powdered charcoal. Tin, in particular, is not easily reduced to the metallic condition, but the reduction is best accomplished by insuring an intimate mixture with the charcoal.

VII. *Borax beads.*—The beads give best results when very small amounts of the material, in solid form, are used.

VIII. *Flame tests.*—The graphite point is conveniently made by sharpening a lead-pencil to a large, flattened blade. It has the advantage over platinum that it cannot be injured by reducible substances, such as copper or arsenic compounds. Care should be taken to use a clean surface of the graphite for each test. Substances which do not adhere readily to the graphite may be made to do so by wetting the blade.

PREPARATION FOR ANALYSIS.

A. SOLIDS.

Treatment with Water.

Put about 0.2 grm. of the substance in a test-tube, add about 10 cm.^{3} of water, and boil if necessary. If the substance is soluble, proceed with the *Analysis*. For the basic ions, the solution may be analyzed at once according to the procedure of the *Basic Analysis*. In testing for the acidic ions the only basic ions which should, in general, be present are those of the alkali metals, sodium and potassium. If, therefore, the original substance is soluble in water and contains no organic matter (found in the *Preliminary Testing* or in the *Basic Analysis*) which may interfere in the precipitation of a base by an alkali carbonate, add sodium carbonate in excess and boil the liquid. If ammonium salts are present, the boiling is continued with suitable addition of the carbonate until all the ammonia is set free and volatilized; then filter. The filtrate free from everything which can interfere (excepting *As*, *Sb*, and traces of other metallic ions) in testing for acidic ions, and conveniently designated the *Prepared Solution*, is treated in many individual portions by the methods of the *Acidic Analysis*.

If the substance contains objectionable organic matter, it must be fused with Na_2CO_3. The fused mass is treated with water, the liquid filtered, and the filtrate reserved for individual tests for the acids. The fusion process, besides destroying objectionable organic matter, may change or destroy certain acidic ions (*e.g.*, the ions of nitric, nitrous, oxalic, tartaric, sulphurous, thiosulphuric, chloric acids), and such acidic ions must be sought especially in the original substance. Some peculiar combinations are also liable to change under the fusion process; such possible changes must be studied specially in each individual analysis.

A comparison of the results of the *Basic Analysis* with the data of the *Table of Solubilities* on pp. 126, 127 may serve to shorten the processes of the *Acidic Analysis* by eliminating tests for certain acidic ions which form only insoluble compounds with the basic ions already discovered.

If the substance is wholly or partly insoluble in water, decant the supernatant liquid from the insoluble material, filter, and evaporate a few drops. The formation of a residue indicates a substance partly soluble in water. The water solution may be analyzed by the procedure just described; the insoluble material must be treated by the following process:

Treatment with Acids.

(*a*) Put 3 or 4 $cm.^3$ of dilute HCl upon the material and boil, noting carefully any phenomena attending the solution of the substance, such as evolution of gas, change of color, etc. If the substance dissolves, dilute the solution and proceed as directed in the *Basic Analysis*, noting that the ions Ag and Hg_2, which form insoluble chlorides, may not be present.

(*b*) If the substance does not dissolve in dilute HCl, treat it with 3 or 4 $cm.^3$ of strong HCl and boil. If complete solution is effected at once, or upon dilution with water, proceed as directed in the *Basic Analysis*.

(*c*) If HCl does not bring about solution, try the effect of 3 or 4 $cm.^3$ of HNO_3 (evolution of red fumes denotes oxidation). If solution is secured, with or without subsequent dilution with water, evaporate the excess of free HNO_3 so far as possible, dilute sufficiently, and proceed as directed in the *Basic Analysis.*

(*d*) If neither HCl nor HNO_3 effects solution by itself, try the action of aqua regia (three parts HCl to one part HNO_3). If solution is effected with or without addition of water, evaporate the free acid so far as possible, dilute, and proceed as directed in the *Basic Analysis.*

(*e*) If neither HCl nor HNO_3 nor aqua regia effects the complete solution of the substance, dilute sufficiently and separate the liquid from the insoluble residue. The liquid may be examined for material in solution, as directed in the *Basic Analysis.* The *insoluble residue* is to be handled according to the *Special Treatment of Substances Insoluble in Water and Acids.*

Before the tests for the acidic ions are made, the basic ions are to be removed as described under the *Treatment with Water* above; and it must be borne in mind that either HCl, HNO_3, or a mixture of these acids was used in getting the substance into solution. If HCl was used, the second group of acidic ions may perhaps be tested for by making a solution of the substance in HNO_3; if HNO_3 was used, the third group may be tested for by dissolving as much as will dissolve in HCl, and using the solution for the test.

Here also reference to the *Table of Solubilities* is most useful.

Special Treatment of Substances Insoluble in Water and Acids.

The commonly occurring substances insoluble in water and acids which we shall consider are: $AgCl$; $AgBr$; AgI; $AgCN$; $Ag_4FeC_6N_6$; $Ag_3FeC_6N_6$; $PbSO_4$; $BaSO_4$; $SrSO_4$; $CaSO_4$; Al_2O_3; Cr_2O_3; $FeCr_2O_4$; CaF_2; S; C; SnO_2; Sb_2O_4; SiO_2, and many silicates. These must be examined by special methods.

Test the substance insoluble in acids in different portions:

(*a*) Look for S as in the *Preliminary Testing.* (If the preliminary examination has been thoroughly made, the examination for S need not be repeated at this point.)

(*b*) Look for C as in the *Preliminary Testing.* In general, C may be confirmed by noting the black color of the substance and its combustion in a current of air with formation of CO_2.

(*c*) To test the substance for *Sn* and *Sb* present as insoluble oxides, the substance is to be fused in porcelain with three times its weight of Na_2CO_3 intermixed thoroughly with an equal amount of sulphur. Water extracts from the fused mass *Sn* and *Sb* as sulpho-salts, and from the solution the sulphides may be thrown down by HCl and identified as usual.

(*d*) Test for CN, $Fe^{II}C_6N_6$, and $Fe^{III}C_6N_6$ in compounds insoluble in water and acid, by boiling with a strong solution of NaOH or KOH. Dilute, filter, acidify the filtrate with HCl, and test for the cyanides as directed in the *Acidic Analysis.*

(*e*) Test for the halides of *Ag* by adding Zn and dilute H_2SO_4 to the substance in a crucible and allowing to stand a few minutes. Filter, dissolve the residue in HNO_3, and test for *Ag* as directed in the *Basic Analysis;* test the filtrate for Cl, Br, and I as directed in the *Acidic Analysis.*

(*f*) Test for *Pb* and SO_4 in $PbSO_4$ by boiling with a concentrated solution of $NH_4C_2H_3O_2$, filter, divide.

(1) Add K_2CrO_4—P. yellow $PbCrO_4$ indicates *Pb.*

(2) Acidify with HCl, filter if necessary, add $BaCl_2$. Test precipitate for SO_4 by action on silver coin (see Group I, *Acidic Analysis*).

(*g*) If either S or C has been found, it must be removed by roasting. Then fuse the residue with four times its weight of a mixture of Na_2CO_3 and K_2CO_3 taken in equal parts. Make the fusion on a thin *iron* sheet; continue to heat until all effervescence ceases; extract the mass remaining (well broken up) with boiling water, filter and wash, and examine the residue and filtrate separately.

(*a*) *Filtrate.*	(*b*) *Residue.*
Acidify with dilute HCl and evaporate to dryness. Desiccate the residue at a temperature not much exceeding that of boiling water (*e.g.*, 110°), treat the dried residue with a few drops of strong HCl and then with hot water, and filter. Test the residue for silica by the sodium-metaphosphate bead, or by mixing with a fluoride, treating with H_2SO_4, and bringing the fumes evolved into contact with a moistened rod. Test the filtrate for *Al* and Si.	Dissolve so far as possible in dilute HNO_3, evaporate to dryness in porcelain, desiccate as in (*a*) to make the SiO_2 insoluble. Treat dried residue with a few drops of HNO_3 and then with hot water, filter, and test filtrate in the usual manner for *Ag, Pb, Al,* (*Ca*), *Mg,* and Si.

(*h*) Fuse another portion of the substance with four times its weight of a mixture of Na_2CO_3 and K_2CO_3 in equal parts, to which has been added an amount of KNO_3 equal to that of the substance. If *Pb* or *Ag* has been found, this fusion is to be made in porcelain; if neither *Pb* nor *Ag* is present, fusion may be safely and best made in platinum. Extract the fused mass thoroughly with hot water and wash upon the filter.

(1)	(2)	(3)
(*a*) Acidulate a portion of the filtrate with $HC_2H_3O_2$, and test with $Pb(C_2H_3O_2)_2$ for *Cr*, which is now present (if present at all) in the form of chromic acid. (*b*) Acidulate with HCl and test for the acidic ions of I and III, as directed in the *Acidic Analysis*. (*c*) Acidulate with HNO_3 and test for the acidic ions of Group II, as directed in the *Acidic Analysis*.	The portion of the fused mass insoluble in hot water is to be treated with dilute HCl, evaporated, and dried to remove the SiO_2. The solution obtained after separating the silica may be tested for *Fe* and other bases, except those present in porcelain. The alkali ions *Na*, *K*, and *Li* are to be tested for by method (*j*).	If fusion was made in platinum, *Al* may also be tested for both in the filtrate and in the residue after extraction with water.

(*i*) To determine the condition of oxidation of the iron, the original substance must be dissolved out of contact with air. For this purpose the substance may generally be treated in a trapped flask with strong boiling HCl, or, in case of insoluble silicates, the substance may be dissolved (in a lead or platinum dish) in a mixture of sulphuric and hydrofluoric acids. In either case the condition of *Fe* may be recognized in the diluted solution by the usual tests.

(*j*) Alkalies present in the insoluble silicates are best found by thoroughly mixing the finely pulverized substance with an equal amount of NH_4Cl and eight times its weight of $CaCO_3$, heating the mixture in platinum to bright redness for about three-quarters of an hour, extracting the fritted residue with water, precipitating with $(NH_4)_2CO_3$, evaporating the filtrate to small bulk, again treating with $(NH_4)_2CO_3$, filtering, evaporating to dryness and igniting to remove ammonium salts, dissolving in a few drops of water and a drop of HCl, and testing before the spectroscope.

B. LIQUIDS AND SOLUTIONS.

(*a*) If the liquid or solution is *neutral* to litmus, proceed as directed in the *Basic Analysis* and in the *Acidic Analysis*.

(*b*) If the liquid or solution is *acid* to litmus, remove, if necessary, as much free acid as possible, and proceed as directed in the *Basic Analysis* and in the *Acidic Analysis*.

(*c*) If the liquid or solution is *alkaline*, acidify with HNO_3 carefully. If no precipitate forms, proceed as directed in the *Basic Analysis* and in the *Acidic Analysis*. If a precipitate falls, filter, and proceed to examine the filtrate as directed in the *Basic Analysis* and in the *Acidic Analysis* and prepare the residue according to the methods laid down in A.

C. GASES.

Gases can be completely and properly analyzed only by the special methods, chiefly quantitative, of *gas analysis*.

COMMENTARY UPON THE PREPARATION FOR ANALYSIS.

I. Treatment with water.—It is assumed that the *Preliminary Testing* has preceded, and that the phenomena observed have been duly studied. If this is the case, any special phenomena, such as the evolution of gas, change of color, etc., attending the action of water upon the substance have been interpreted. The application of the *Basic Analysis* and the *Acidic Analysis* follows then in due course.

The basic ion or ions present having been determined, a reference to the *Table of Solubilities* will shorten the examination for the acidic ions, by the elimination of those acidic ions which form with the basic ions present insoluble compounds. For example, should barium be the basic ion found, practically all the acidic ions of Group I are shown to be absent.

The removal of the basic ions before testing for the acidic ions is not always necessary, but it is advisable, because in many instances the presence of basic ions does interfere in the tests for the acidic ions. In removing the basic ions by boiling with sodium carbonate, a large excess of that reagent is to be avoided, both on account of its solvent action upon certain of the precipitates thus formed, and also because of the undesirability of having considerable amounts of it in the *Prepared Solution*. After the basic ion present is known, proper precautions in the use of sodium carbonate will naturally suggest themselves.

II. Treatment with acids.—It is very important to note any phenomena that occur in connection with the action of acid upon the substance insoluble in water. If a carbonate or sulphide, for example, should be under examination, carbon dioxide or hydrogen sulphide would be evolved as soon as the acid was added, and unless promptly tested for would be lost.

Any considerable excess of acid remaining after the treatment with acid should be removed by evaporation. An excess of hydrochloric acid tends to prevent the precipitation of certain of the sulphides by hydrogen sulphide, and an excess of nitric acid not only tends to form aqua regia when hydrochloric acid is added, but oxidizes hydrogen sulphide to sulphuric acid and sulphur.

Acidic ions which give, with the basic ions found, compounds soluble in water are not to be looked for; and it is perhaps unnecessary to add that the acidic ion of any acid used in making a solution of the substance is not to be tested for in that solution.

III. Special treatment of substances insoluble in water and acids.—(*a*) and (*b*) Many of the commonly occurring substances insoluble in water and acids, such as sulphur and carbon, will have been identified by the *Preliminary Testing.*

(*c*) By fusion of the oxides of tin and antimony with sodium carbonate and sulphur, the sulpho-salts sodium sulphostannate and sodium sulphantimonate are formed. These are decomposed by hydrochloric acid with formation of sulphides, which in turn are acted upon by stronger hydrochloric acid with production of soluble chlorides.

(*d*) When the insoluble cyanides are acted upon by strong potassium hydroxide or sodium hydroxide, the insoluble hydroxides or oxides of the metals and the soluble cyanide of sodium or potassium are formed.

(*e*) The action of zinc and sulphuric acid upon the halides of silver is to throw out the silver on the zinc and liberate the halogen acid.

(*f*) Ammonium acetate, acting upon lead sulphate, forms lead acetate and ammonium sulphate.

(*g*) The fusion on iron is made particularly for the detection of silver, lead, aluminium, and silicon. Should silver or lead be present, it would not be safe to use platinum on account of the danger of forming a fusible alloy with the platinum; and a fusion in porcelain would probably introduce some aluminium and silicon, both of which are present in porcelain. The potassium carbonate and the sodium carbonate are mixed, because fusion is effected at a lower temperature than that at which either of these carbonates fuses alone. It is important to extract the fused mass thoroughly with boiling water, in order to insure a complete separation between the soluble and the insoluble materials.

(*h*) This fusion is made in platinum or porcelain, according to the results of the previous fusion on iron. The potassium nitrate or the sodium peroxide is used to convert any Cr^{III} present to Cr^{VI}. The acidic ions in general are to be found in the hot-water extract after fusion; the basic ions are generally to be found in the residue from the hot-water treatment. Some SiO_4 usually remains with the basic ions in the residue after treatment with water, and some soluble compounds of aluminium may be found in the hot-water extract.

TABLE SHOWING THE SOLUBILITY OF

	O	S	Cl	Br	I	CN	CrO_4	AsO_3	AsO_4	SO_4	PO_4	BO_3	C_2O_4
K	1	1	1	1	1	1	1	1	1	1	1	1	1
Na	1	1	1	1	1	1	1	1	1	1	1	1	1
NH_4	1	1	1	1	1	1	1	1	1	1	1	1	1
Ba	1	1	1	1	1	1–2	2	2	2	3	2	2	2
Sr	1	1	1	1	1	1	1–2	2	2	3	2	2	2
Ca	1–2	1	1	1	1	1	1–2	2	2	1–3	2	2	2
Mg	2	2	1	1	1	1	1	2	2	1	2	1–2	2
Al	2 & 3	2	1	1	1	. .	. .	. .	2	1	2	2	2
Cr	2 & 3	2 & 3	1 & 3	1 & 3	1	2	2	. .	2	1 & 2	2	2	1–2
Fe^{III}	2	2	1	1	1	. .	1	2	2	1	2	2	2
Fe^{II}	2	2	1	1	1	2–3	. .	2	2	1	2	2	2
Zn	2	2	1	1	1	2	1	. .	2	1	2	2	2
Mn	2	2	1	1	1	2	1	2	2	1	2	2	1–2
Ni	2	2	1	1	1	2–3	2	2	2	1	2	2	2
Co	2	2	1	1	1	2–3	2	2	2	1	2	2	2
Ag	2	2	3	3	3	3	2	2	2	1–2	2	2	2
Pb	2	2	1–3	1–3	1–2	2	2–3	2	2	2–3	2	2	2
Hg_2	2	2	2–3	2–3	2	. .	2	2	2	1*	2	. .	2
Hg	2	2	1	1	2	1	1–2	2	2	1*	2	. .	2
Bi	2	2	1–2	1–2	2	. .	2	. .	2	1*	2	2	2
Cu	2	2	1	1	1	2	1	2	2	1	2	3	2
Cd	2	2	1	1	1	2	2	. .	. .	1	2	1–2	2
Sn^{II}	2	2	1	. . .	1	. .	2	. .	. .	1	2	2	2
Sn^{IV}	2 & 3	2	1	. . .	1	. .	. .	. .	2	. . .	2	. .	1
Sb	2	2	1*	1*	1*	. .	2	2	2	2	1–2	. .	2

1 = soluble in water.
2 = “ “ acids only.
3 = insoluble in water and acids.
1–2 = sparingly soluble in water, readily in acids.
1–3 = “ “ “ “ and acids.
2–3 = “ “ “ acids only.

COMMON SALTS IN WATER AND ACIDS.

F	CO_3	SiO_4	$C_4H_4O_6$	$Fe^{II}(CN)_6$	$Fe^{III}(CN)_6$	NO_3	ClO_3	$C_2H_3O_2$	NO_2	ClO	SCN	SO_3	S_2O_3	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	*K*
1	1	1	1	1	1	1	1	1	1	1	1	1	1	*Na*
1	1	..	1	1	1	1	1	1	1	1	1	1	1	*NH_4*
2–3	2	2	2	1–2	..	1	1	1	1	1	1	2	1–2	*Ba*
2–3	2	2	2	1	..	1	1	1	1	1	1	2	1	*Sr*
2–3	2	2	2	1	1	1	1	1	1	1	1	2	1	*Ca*
2–3	2	2	1–2	1	1	1	1	1	1	1	1	..	1	*Mg*
1	..	2–3	1	..	..	1	1	1	..	..	..	..	..	*Al*
1	..	2	1	..	..	1	1	1	..	..	..	..	..	*Cr*
1	..	2	1	3	1	1	1	1	..	..	1	..	..	*Fe^{III}*
1–2	2	2	1–2	3	3	1	1	1	..	..	1	..	..	*Fe^{II}*
1–2	2	2	2	2–3	2	1	1	1	..	..	1	..	..	*Zn*
2	2	2	1–2	2	3	1	1	1	..	..	1	..	..	*Mn*
1–2	2	2	2	3	3	1	1	1	..	..	1	..	..	*Ni*
1–2	2	2	1	3	3	1	1	1	..	..	1	..	..	*Co*
1	2	..	2	3	3	1	1	1	1–2	1	..	2	1–2	*Ag*
2	2	2	2	2	1–2	1	1	1	..	..	..	2	1–2	*Pb*
..	2	..	1–2	..	..	1*	1	1–2	..	..	..	..	..	*Hg_2*
1–2	2	..	2	..	..	1*	1	1	..	..	1	..	..	*Hg*
1	2	..	3	..	..	1*	1	1	..	..	..	..	..	*Bi*
2	2	2	1	3	..	1	1	1	..	..	1	..	..	*Cu*
1–2	2	2	1–2	..	..	1	1	1	..	..	..	..	..	*Cd*
1	..	..	2	3	3	..	1	1	..	..	..	..	..	*Sn*
1	..	..	..	3	..	..	..	1	..	..	..	..	..	*Sn^{IV}*
1	..	..	3	..	..	..	..	..	..	..	..	..	..	*Sb*

Places left blank correspond to salts which are uncommon, difficult to prepare, indefinite, or unknown.

* Acted upon by water with the formation of insoluble basic salts.

PART V.

ORGANIC COMPOUNDS.

THE ELEMENTARY ANALYSIS.

Given a pure compound of carbon, the elementary analysis is a comparatively simple matter. Those compounds will be considered which, besides carbon, may contain the elements hydrogen, oxygen, nitrogen, sulphur, phosphorus, and the halogens.

(1) **Carbon and Hydrogen.**—If the substance is not easily volatilized, mix a small amount of it with powdered CuO, previously ignited, in a test-tube fitted with a mushroom-trap moistened with lime-water, and heat strongly. If the substance is a volatile solid or liquid, saturate with it asbestos fiber, cover with CuO, and proceed as in the preceding experiment. If the substance is a gas, allow it to pass from the container into a U tube containing red-hot CuO and fitted with a mushroom-trap moistened with lime-water. Turbidity, due to the formation of $CaCO_3$, indicates C, moisture in the cooler parts of the tube indicates H.

(2) **Nitrogen.**—(*a*) Bring the substance, solid, liquid, or gas, *cautiously* into contact with a small amount of melted sodium just as it was brought into contact with CuO in the

preceding test. Project (with caution) the hot tube into a beaker containing about 25 cm.^{3} of water, boil, filter, add to the filtrate a solution of $FeSO_4$ and $FeCl_3$, make alkaline with NaOH, boil again, and acidify with HCl—Prussian blue $Fe^{III}{}_4(Fe^{II}C_6N_6)_3$ indicates N.

(*b*) Bring the substance into contact with a large quantity of soda-lime (Na_2CO_3 and CaO taken in equal parts). The odor of NH_3 or blue coloration of red litmus by volatile gas indicates N.

(3) **Sulphur.**—(*a*) Treat with sodium as in (2), (*a*). After extracting with water and filtering, divide the solution. (1) To one portion add a few drops of a solution of sodium nitroprusside $Na_2Fe(CN)_5(NO)$. A violet color indicates S. (2) To the other portion add $Pb(C_2H_3O_2)_2$ and $HC_2H_3O_2$. Black PbS indicates S.

(*b*) Bring the substance, solid, liquid, or gas, cautiously into contact with fused $K_2Cr_2O_7$, or with a fused mixture of Na_2CO_3 and Na_2O_2 or KNO_3. Extract the cooled mass with water, filter, acidify with HCl, and add $BaCl_2$. A white precipitate, $BaSO_4$, indicates S.

(4) **Phosphorus.**—Bring the substance, as in (3), into contact with a fused mixture of Na_2CO_3 and Na_2O_2 or KNO_3, extract the cooled mass with water, filter, acidify strongly with HNO_3; and add ammonium molybdate, $(NH_4)_2\ MoO_4$. The formation of yellow $(NH_4)_3PO_4.11MoO_3.6H_2O$ indicates P.

(5) **The Halogens.**—Heat the substance with CaO in a test-tube, cool, extract with water, filter, acidify with HNO_3, and add $AgNO_3$. A precipitate (AgCl, AgBr, AgI) indicates Cl, Br, or I.

CHARACTERISTIC REACTIONS OF A FEW COMMON ORGANIC ACIDS.

Reagents.	*Formic Acid,* $HCOOH$.	*Acetic Acid,* CH_3COOH.	*Oxalic Acid,* $(COOH)_2$.	*Tartaric Acid,* $(CH_2)(OH)_2(COOH)_2$	*Citric Acid,* $(CH_2)_2COH(COOH)_3$
H_2SO_4, *conc.*	CO in the cold. Burns with blue flame.	Characteristic odor, similar to vinegar.	CO and CO_2 on warming.	Immediate charring with burnt-sugar odor. On warming CO, CO_2, and SO_2 evolved.	Chars slowly on warming. CO, CO_2, and SO_2 evolved.
H_2SO_4+ *alcohol*	Odor of ethyl formate, similar to chloroform.	Odor of ethyl acetate.	....	....	....
$AgNO_3$	Gray silver by reduction. Best obtained on heating.	White precipitate in concentrated solution. Not reduced on boiling.	White crystalline precipitate soluble in NH_4OH and HNO_3.	White precipitate. Reduced in NH_4OH solution.	White curdy precipitate. Not reduced readily.
$FeCl_3$	Red coloration bleached by HCl. Basic salt on boiling.	Red coloration bleached by HCl. Basic salt on boiling.	....	In neutral solution gives on warming yellow crystalline precipitate.	....
$CaCl_2$	....	....	White precipitate in neutral or acetic-acid solution.	White precipitate in neutral solution. Soluble in $HC_2H_3O_2$ and cold KOH.	In neutral solution precipitate forms slowly in the cold, more readily on boiling.

CHARACTERISTIC REACTIONS OF A FEW COMMON ORGANIC ACIDS (*Continued*).

Reagents.	*Formic Acid,* $HCOOH$.	*Acetic Acid,* CH_3COOH.	*Oxalic Acid,* $(COOH)_2$.	*Tartaric Acid,* $(CH_2)(OH)_2(COOH)_2$	*Citric Acid,* $(CH_2)_2COH(COOH)_3$
Special tests	$HgCl_2$ reduced to Hg_2Cl_2 or Hg on warming.	On heating a dry acetate with As_2O_3 characteristic odor of cacodyl oxide is obtained.	$KMnO_4$ in presence of H_2SO_4 bleached with evolution of CO_2.	(1) $FeSO_4+H_2O+KOH$ in excess, violet to blue coloration. (2) Resorcin and strong H_2SO_4 give on warming red coloration.	$CdCl_2$ gives jelly-like precipitate. Resorcin and pyrogallol give no color.

Reagents.	*Benzoic Acid,* C_6H_5COOH.	*Salicylic Acid,* $C_6H_4(OH)COOH$.	*Uric Acid,* $C_5H_4N_4O_3$.	*Meconic Acid,* $C_3H(OH)(COOH)_2O_2$.	*Gallic Acid,* $C_6H_2(OH)_3COOH$.	*Tannic Acid,* $C_{14}H_{10}O_9$.
H_2SO_4, conc.	Dissolves without charring.	Dissolves, charring slowly.	Dissolves in cold. On warming CO, CO_2, and SO_2 evolved.	....	Green color changing to purple.	Tannic acid is precipitated.
H_2SO_4+ alcohol	Odor of ethyl benzoate.	With methyl alcohol odor of oil of wintergreen.	....	....	....	....
AgNO	In neutral solution white precipitate. Soluble in hot water and NH_4OH.	In neutral solution white precipitate. Soluble in hot water.	....	Light-yellow flocculent precipitate. Soluble in NH_4OH	....	....

CHARACTERISTIC REACTIONS OF A FEW COMMON ORGANIC ACIDS (*Continued*).

Reagents.	*Benzoic Acid,* C_6H_5COOH.	*Salicylic Acid,* $C_6H_4(OH)COOH$.	*Uric Acid,* $C_5H_4N_4O_3$.	*Meconic Acid,* $C_3H(OH)(COOH)_2O_2$.	*Gallic Acid,* $C_6H_2(OH)_3COOH$.	*Tannic Acid,* $C_{14}H_{10}O_9$.
$FeCl_3$	In neutral solution buff-colored precipitate of basic salt. Soluble in NH_4OH.	In neutral solution violet-red color.	....	Purplish brown color. Basic precipitate on boiling.	Blue precipitate. Soluble in excess, forming a green solution.	Bluish black precipitate of ferric-gallo tannate.
$CaCl_2$	....	....	....	White silky precipitate.	....	....
Special tests	Heat with soda-lime, pass vapor into conc. HNO_3. Dilute with water and note odor of nitrobenzene.	Heat with HNO_3 and add NaOH. Note yellow color due to formation of picric acid.	Add HNO_3 and evaporate on water-bath—yellow or reddish brown. Add NH_4OH—violet, NaOH—deep blue.	$Pb(C_2H_3O_2)_2$ gives light-yellow precipitate. Insoluble in $HC_2H_3O_2$. Soluble in HNO_3.	$FeSO_4$ gives azure-blue or purple coloration. Lime-water gives blue precipitate.	$FeSO_4$ gives blackish violet coloration. Lime-water gives gray precipitate.

Reagent.	*Lactic Acid,* $CH_3.CH(OH)COOH$.	*Malic Acid,* $(CH_2)_2CH(OH)(COOH)_2$	*Succinic Acid,* $(CH_2)_2(COOH)_2$.	*Cinnamic Acid,* $C_6H_5CH.CHCOOH$.	*Hippuric Acid,* $C_6H_5CO.NH.CH_2COOH$
H_2SO_4 *conc.*	Gas evolved in the cold. On heating chars and CO evolved.	....	Dissolves in the cold without charring. Chars on heating.	Chars on heating.	....

CHARACTERISTIC REACTIONS OF A FEW COMMON ORGANIC ACIDS (*Concluded*).

	Lactic Acid, $CH_3.CH(OH)COOH.$	*Malic Acid,* $(CH_2)_2CH(OH)(COOH)_2$	*Succinic Acid,* $(CH_2)_2(COOH)_2.$	*Cinnamic Acid,* $C_6H_5CH.CHCOOH.$	*Hippuric Acid,* $C_6H_5CO.NH.CH_2COO$
H_2SO_4+ *alcohol*	....	....	....	....	....
$AgNO_3$	Metallic silver separates slowly.	....	In neutral solution white precipitate, soluble in NH_4OH.	In neutral solution white precipitate.	In neutral solution white curdy precipitate soluble in hot water. Separates out slowly on cooling.
$FeCl_3$	....	....	In neutral solution light-brown precipitate of basic salt.	In neutral solution light-yellow precipitate of basic salt.	In neutral solution brownish pink precipitate. Soluble in alcohol.
$CdCl_2$	....	No precipitate in the presence of an excess of NH_4Cl and NH_4OH.	In neutral solution tardy white precipitate.	In neutral solution white precipitate. Soluble in hot water, crystallizing on cooling.	....
Special tests	Bleaches $KMnO_4$ with effervescence. Odor of acetaldehyde.	$Pb(C_2H_3O_2)_2$ gives white precipitate of lead malate soluble in hot water.	....	$KMnO_4$ in alkaline solution gives odor of benzaldehyde.	(1) Heated with soda-lime gives NH_3. (2) Boiled with 50% NaOH solution gives benzoic acid.

Identification of Organic Acids.

The following methods may be helpful in identifying any single one of the Organic Acids studied.

Method I.

Treat the dry substance with a few cubic centimeters of strong H_2SO_4 and warm gently.

(1) Odor of vinegar indicates *acetic acid.*

(2) Evolution of gas without charring:

  (*a*) CO indicates *formic acid.*

  (*b*) $CO+CO_2$ indicates *oxalic acid* or *uric acid.* Distinguish by reference to Characteristic Reactions.

(3) Charring, with evolution of gas, indicates *tartaric acid, citric acid, succinic acid, lactic acid,* or *cinnamic acid.**

  Distinguish by reference to Characteristic Reactions.

(4) Solution with little or no charring indicates *benzoic acid, salicylic acid, meconic acid, malic acid,* or *hippuric acid.*

  Distinguish by reference to Characteristic Reactions.

(5) A precipitate indicates *tannic acid* (in absence of inorganic bases).

(6) Green coloration changing to purple indicates *gallic acid.*

---

* Cinnamic acid chars without apparent evolution of gas.

Method II.

Treat a small amount of the dry substance with an equal amount of soda-lime and heat.

(1) Evolution of inflammable gases indicates *formic acid, acetic acid, oxalic acid, benzoic acid,* or *cinnamic acid.*

Distinguish by reference to Characteristic Reactions.

(2) Evolution of ammonia indicates *uric acid* or *hippuric acid.*

Distinguish by reference to Characteristic Reactions.

(3) Odor of phenol indicates *salicylic acid.*

(4) None of the above reactions indicates *tartaric acid, citric acid, meconic acid, gallic acid, tannic acid, lactic acid, malic acid,* or *succinic acid.*

Distinguish by reference to Characteristic Reactions.

CHARACTERISTIC REACTIONS OF A FEW COMMON ALCOHOLS.

Reagent.	*Methyl Alcohol,* CH_3OH.	*Ethyl Alcohol,* C_2H_5OH.	*Amyl Alcohol,* $C_5H_{11}OH$	*Pyrogallol,* $C_6H_3(OH)_3$.	*Phenol,* C_6H_5OH.
$H_2SO_4 + HC_2H_3O_2$.	Odor of methyl acetate.	Odor of ethyl acetate.	Odor of amyl acetate.	....	....
$FeCl_3$.	....	....	....	Reddish brown coloration.	Deep violet coloration destroyed by HCl.
$K_2Cr_2O_7 + H_2SO_4$.	Formic acid produced.	Acetaldehyde formed.	Amyl valerianate formed.	....	....
Special tests.	Add a formate, H_2SO_4 conc., and warm—characteristic odor of methyl formate.	Add a crystal of iodine, a little KOH, and warm—odor of iodoform.	Add equal volume of H_2SO_4 conc., half volume of glacial acetic acid, and a little $FeCl_3$—violet coloration.	Add $FeSO_4$—blue coloration.	Add NH_4OH and bromine-water—indigo-blue color turning red on addition of HCl.

CHARACTERISTIC REACTIONS OF A FEW COMMON CARBOHYDRATES.

REAGENT,	*Grape-sugar.*	*Cane-sugar.*	*Milk-sugar.*	*Maltose.*	*Starch.*
H_2SO_4 *conc.*	Does not char in cold.	Chars in cold.	Does not char in cold.	Does not char in cold.	Chars on heating.
KOH or *NaOH hot.*	Brown coloration. Odor of burnt sugar on addition of HNO_3.	....	Same as grape-sugar.	Same as grape-sugar.	....
$Pb(C_2H_3O_2)_2$ $+NH_4OH$.	Precipitate salmon-pink. Soluble in excess of NH_4OH.	Precipitate white.	Precipitate yellowish pink.	Same as milk-sugar.	....
Fehling's solution.	Red Cu_2O by reduction.	....	Red Cu_2O by reduction.	Red Cu_2O by reduction.	....
$Cu(C_2H_3O_2)_2$ $+HC_2H_3O_2$ *boiling.*	Red Cu_2O.	....	....	....	....

CHARACTERISTIC REACTIONS OF A FEW COMMON ALKALOIDS.

ALKALOID.	*I+KI.*	*NaOH* or *KOH.*	*NaHCO₃.*	*Special tests.*
Morphine $\overset{+}{\mathit{Mo}}$	Brown ppt.	No ppt. in excess of precipitant.	No ppt. in acid solution.	$FeCl_3$ on a crystal gives dirty green color.
Narcotine $\overset{+}{\mathit{Na}}$.	" "	White ppt. insol. in excess.	Immediate ppt. even in acid solution.	(*a*) Chlorine water on solution gives yellow-green intensified by NH_4OH. (*b*) A drop of HNO_3 on a crystal dissolved in H_2SO_4 on diluting and warming gives red color.
Quinine $\overset{+}{\mathit{Q}}$.	" "	" "	Tardy ppt. (flocky) even in acid solution.	(*a*) Solution in H_2SO_4 gives blue fluorescence on diluting. (*b*) Solution treated with chlorine water and NH_4OH gives emerald-green. (*c*) Solution treated with chlorine water, $K_4FeC_6N_6$, and NH_4OH gives deep-red tint.
Cinchonine $\overset{+}{\mathit{Ci}}$.	" "	" "	Tardy ppt. (crystalline) even in acid solution.	A drop of HNO_3 on a crystal dissolved in cold H_2SO_4 gives, on warming, yellow, dark red to black.
Strychnine $\overset{+}{\mathit{Sr}}$.	" "	" "	No ppt.	MnO_2 added to a crystal covered with H_2SO_4 (on porcelain) gives purple color changing to wine-red and finally reddish yellow.
Brucine $\overset{+}{\mathit{Br}}$.	" "	" "	" "	Strong HNO_3 gives to solution intense red color, changing to violet on warming, diluting and adding $(NH_4)_2S$.
Veratrine $\overset{+}{\mathit{Ve}}$.	" "	" "	" "	(*a*) H_2SO_4 on a crystal gives, on warming, yellow color changing to reddish yellow, deep red, purple red. (*b*) Strong cold HCl on crystal gives no color; on warming purple or wine-red.
Atropine $\overset{+}{\mathit{At}}$.	" "	" "	" "	No color tests.

THE IDENTIFICATION OF A SINGLE ALKALOID.

Dissolve a small crystal of the alkaloid in a few drops of water, adding a drop of dilute H_2SO_4.

I. To a drop of solution add KI+I.
- P. brown indicates possible presence of a member of this group.
- No P. indicates absence of this group.

II. To a drop of solution add KOH or NaOH in excess.
- P. white indicates $\overset{+}{\text{Na}}$, $\overset{+}{\text{Q}}$, $\overset{+}{\text{Ci}}$, $\overset{+}{\text{Sr}}$, $\overset{+}{\text{Br}}$, $\overset{+}{\text{Ve}}$, or $\overset{+}{\text{At}}$.
- No P. indicates $\overset{+}{\text{Mo}}$. Confirm by $FeCl_3$; dirty green color.

III. If a precipitate was obtained in II add to a fresh portion of original solution a few drops of a solution of $NaHCO_3$ and allow to stand for some time.
- P.
  - Immediate indicates $\overset{+}{\text{Na}}$.; (*a*) confirm by chlorine water and NH_4OH—yellow-green.
    (*b*) confirm by H_2SO_4 and HNO_3 (warming)—red color.
  - Tardy and flocky indicates $\overset{+}{\text{Q}}$.; (*a*) confirm by chlorine water and NH_4OH—emerald-green.
    (*b*) confirm by chlorine water, $K_4FeC_6N_6$ and NH_4OH—red color.
    (*c*) confirm by H_2SO_4 and dilution—blue fluorescence.
  - Tardy and crystalline indicates $\overset{+}{\text{Ci}}$.; confirm by H_2SO_4, HNO_3 and warming—yellow, red, to black.
- No P.
  - $\overset{+}{\text{Sr}}$. MnO_2, H_2SO_4 upon crystal of original substance gives purple to wine-red.
  - $\overset{+}{\text{Br}}$. HNO_3 gives intense red when added to original solution; and diluting, warming, and adding $(NH_4)_2S$ gives red or violet.
  - $\overset{+}{\text{Ve}}$. HCl upon crystal of original substance gives no color in the cold, on heating purple to wine-red.
  - $\overset{+}{\text{At}}$. No color tests.

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